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16. Abstracts The results of a contractual effort to correlate and evaluate data from several sources, on the development of the alkalized alumina sorbent and process are reported in two phases: Phase I - data evaluation and preliminary process design, and Phase II - process optimization studies. This report includes an analysis of available attrition data, and a summary of the attrition test methods used. The process design study includes an evaluation of; sorption chemistry, current sorption data, and sorption modeling. Regeneration reactions and evaluation of the status of the data are presented with discussion of pilot plant results, bench scale tests with reducing gases, and evaluation of various sorbents. Process description; calculations and vessel design are presented for three process designs; dispersed phase, fluid bed, and fixed bed. A steam reformer, a claus plant and a precipitator, are included for each process. A comprehensive economic analysis of the process is also included.				
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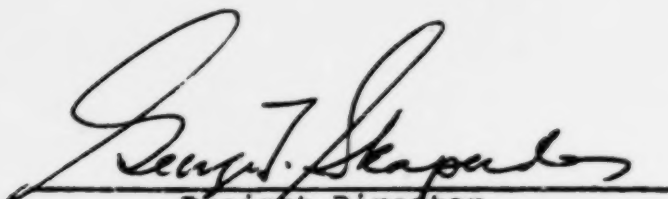
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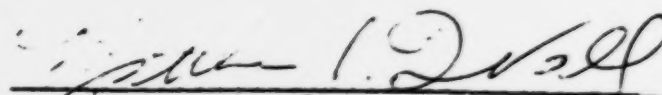
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FEBRUARY 28, 1970

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February 28, 1970

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PREFACE

The work described in this report was performed under Contract No. PH 86-68-86, Department of Health, Education, and Welfare, Public Health Service, Consumer Protection and Environmental Health Service, National Air Pollution Control Administration (NAPCA).

As originally scoped the contract specified three main phases, viz., 1) preliminary studies; 2) process optimization studies; and 3) a conceptual design. This report covers the phases 1 and 2 work. Phase 3 scope was modified substantially and will be a subject of a separate report.

The plant investment and operating costs obtained as a result of the phases 1 and 2 evaluation were unexpectedly high when compared to values previously reported in the literature. Because of these unusually high costs and the lack of success in sorbent development, a reappraisal of the phase 3 work was made which resulted in Kellogg recommending a scope change whereby a cost sensitivity analysis would be substituted for the conceptual design. NAPCA subsequently agreed to the proposed scope change since there appeared to be little value in making a prototype plant design for a high cost process which requires a sorbent that has not yet been successfully developed. On the other hand, the proposed cost sensitivity study would delineate the areas where major cost reductions might be possible and thus provide useful information for guiding future research and development of SO₂ removal schemes.

One of the principal results that should be obtained from the phase 3 study will be the effect on operating costs of such items as load factor, maintenance charges, by-product sulfur selling price and capital charge rate. Many of these items generally do not have one specific "right" value since they vary from site to site, but

a single value of each had to be chosen for the base case economic evaluations of the three process schemes studied in the phases 1 and 2 work. Consequently, the values assigned to these parameters will vary among different investigators so that comparisons of different processes often are not on a common basis. By determining the effect on plant costs of the major parameters over a range of values, as will be done in phase 3, a means for comparing different processes on a common basis will be provided.

The results of the phase 3 work will be presented in the form of graphs and charts such that a range of values for essentially any combination of major parameters may be evaluated. It is presently expected that the phase 3 final report will be published in the spring of 1970.

INTRODUCTION

The invention of the alkalized alumina sorbent and process for removing sulfur oxides from gases is covered by United States patent 2,992,884, July 18, 1961, assigned to the United States of America by the inventors Bienstock and Field. Development of the alkalized alumina sorbent and process resulted from a study started in 1956 by the United States Bureau of Mines (USBM) for the Department of Health, Education, and Welfare. Objectives of the study were the screening of existing processes and, if it appeared feasible, development of new materials or processes which could be used for removing SO₂ from flue gases on a commercial scale. After several years of intensive research during which many potential candidates were evaluated, the alkalized alumina sorbent was selected as having the most potential for commercial application. Consequently, development of the alkalized alumina sorbent and process was undertaken to provide experimental data on which process designs and economics could be based.

To facilitate the development of alkalized alumina, programs were established by several different investigators, viz., AVCO Corporation, W. R. Grace Company, and the USBM both at Bruceton, Pennsylvania and Albany, Oregon. Various aspects of the development were emphasized at the different locations, e.g., sorbent development by Grace, kinetics by AVCO, etc., although some overlap did occur. As the development of alkalized alumina progressed, it became apparent from the mass of data being accumulated that correlation and evaluation of these data by a single contractor was needed. Consequently, The M. W. Kellogg Company was awarded a contract to serve as prime contractor to evaluate the alkalized alumina process. The contract comprised these phases which can be briefly summarized as follows: phase 1 -

data evaluation and preliminary process design; phase 2 - process optimization studies; and phase 3 - a conceptual design for a base case based on the phase 1 and 2 results. This report covers the work done under phases 1 and 2, namely data evaluation, and preliminary process design including process economics. Phase 3 work, for which a scope change has been prepared, will be the subject of a separate report. A cost sensitivity study has been substituted for the prototype plant design specified in the original contract.

SUMMARY

The basic sorbent used in the alkalized alumina process is an activated form of sodium aluminate (NaAlO_2) prepared by thermally driving off water and carbon dioxide from Dawsonite [$\text{NaAl}(\text{CO}_3)(\text{OH})_2$] which in turn has been prepared as a precipitate by reacting liquid solutions of sodium carbonate and aluminum sulfate. After activation the sodium content is about 25%, the surface area is in the range of 50-70 square meters per gram, and the pore volume is about 0.6 cubic centimeters per gram. Small amounts (<1%) of iron in the sorbent are needed to provide adequate regeneration properties; i.e., without iron, the regeneration is incomplete and the rate of regeneration is very slow. Removal of sulfur dioxide by the alkalized alumina is effected by sorption and oxidation to sulfur trioxide and formation of the alkali metal sulfate; i.e., sodium sulfate (Na_2SO_4). Regeneration is accomplished by reacting the sodium sulfate with a reducing gas (e.g., hydrogen steam-reformed methane) thereby converting the sodium sulfate back to sodium aluminate and liberating the sulfur as gaseous hydrogen sulfide. The standard sorbent exhibits one notable deficiency, viz., very low attrition resistance, but sorbent development is the subject of separate studies by others and is not part of the present contract. All the work on the alkalized alumina process done to date by M. W. Kellogg and included in this report is based on the standard alkalized alumina sorbent as described above.

The mechanism of SO_2 removal by alkalized alumina has been studied by various investigators (e.g., USBM, AVCO Corp., W. R. Grace) and several kinetic models have been developed that appear to adequately describe this mechanism based on laboratory and pilot plant data. The various models all agree quite well for the lower range of sorbent loading (i.e., percent sulfur on sorbent), but exhibit some deviations in the upper range. There are some differences in

sorption data reported by different investigators but in general these differences are within the range of experimental accuracy.

Although the actual mechanism by which SO_2 removal is accomplished has not been completely resolved to everyone's satisfaction, the following is a composite of the generally accepted theories. It appears that the SO_2 removal mechanism is pore diffusion controlled when an actual flue gas is being treated, whereas both diffusion and reaction rate are involved when a simulated flue gas is used. The nitrogen oxides (NO_x) in the actual flue gas apparently catalyze the Na_2SO_4 reaction by increasing the SO_2 to SO_3 oxidation rate, such that a shell of Na_2SO_4 is rapidly formed on the outside surface of the sorbent particle. Further, it has been shown that above sorbent loadings of 1-2% sulfur, pure diffusion is controlling. Thus the rate of diffusion of the reactants (i.e., SO_2 , O_2) into the interior of the particles essentially controls the rate of SO_2 removal from the flue gas since the time required for the reaction is negligible. Further, with the higher reaction rate the SO_2 backpressure in the particle interior is essentially zero, thus enhancing the diffusion rate. An alternate theory is that NO_x increases the reaction rate and weakens the shell by causing the formation of a porous Na_2SO_4 shell. All of the above appear reasonable and it is quite possible that the actual mechanism is some combination of the various methods described above. It should be emphasized, however, that while the actual mechanism is important for sorbent development work, for the present study it does not affect process design once adequate sorption models have been developed and confirmed by experimental data.

As pointed out above, the rate of SO_2 removal from actual flue gases is 2 to 3-fold that from simulated flue gases which do not contain NO_x . Since actual flue gases from coal-fired power plants will always contain NO_x , the data and models based on gases containing these two compounds have been used in the present study.

The present goal of SO₂ removal efficiency has been arbitrarily set at 90% based on the SO₂ concentration in the flue gas feed. Reported experimental data show that this goal has been satisfactorily achieved in the fixed and fluid bed systems but has not been adequately demonstrated in the dispersed phase unit. Most of the dispersed phase data show 50-70% SO₂ removal with about 90% removal being achieved in but a few runs. However, an extended steady state run has not been made, primarily due to the lack of an adequate supply of sorbent. It is believed that 90% removal can be achieved with the proper sorbent and perhaps some adjustment of operating conditions if necessary.

The equilibrium level of sulfur on the sorbent after multicycles of sorption-regeneration has not been clearly defined. The initial sulfur content of the activated sorbent is generally less than 1%, but builds up to a higher level after several cycles of sorption-regeneration. The actual level does not significantly affect process design provided (1) the design working level (i.e., the difference in sulfur content between loaded and regenerated sorbent) can be achieved, and (2) the sorption and/or regeneration kinetics are not appreciably reduced. A multicycle test under anticipated operating conditions is required to determine the equilibrium level of sulfur on the sorbent. It is possible that the sorbent sulfur level continues to build up as the number of sorption-regeneration cycles increases, in which case the working differential would be gradually decreased. Long term tests would also resolve this question.

There are various reactions that could describe the regeneration of alkalized alumina but to date, the exact mechanism has apparently not been determined. Some experimental data have been obtained which indicate the regeneration to be exothermic but thermodynamic calculations show that it can also be endothermic. At present there does not appear to be sufficient data available to clearly define the reaction(s). Depending on which of the

several possible reactions occurs, the heat of reaction can be either endo- or exothermic and calculations of the heat balance around the regenerator show that the temperature can vary by 15-50°F, the actual value being a function of the specific regenerator design used. A better definition of the regeneration mechanism would allow the regeneration system to be designed with fewer safety factors than presently used.

The full effect of various process parameters on regeneration has not yet been determined. One of the main problems in present regeneration studies is the fact that a suitable sorbent has not yet been found. Therefore, one of the major process parameters, viz., the effect of regeneration conditions on sorbent attrition resistance, cannot be properly evaluated. In fact, the attrition losses of the presently available sorbents are so high that very little effort has been directed toward measuring the effect of various parameters (e.g., water content of the reducing gas) on attrition resistance since the results would be of doubtful value. Once a suitable sorbent has been developed then optimization studies of regeneration conditions can be made. Meanwhile, present regeneration studies have progressed to the point that several general trends are apparent, as listed below.

The presence of about 1% iron in the sorbent both increases the rate of regeneration gas consumption, and results in more complete sulfur removal. In fact, those sorbents without iron exhibited very slow reaction rates and incomplete sulfur removal to the extent that they would probably not be commercially acceptable.

The gases tested for single step regeneration include hydrogen, carbon monoxide, steam reformed natural gas, producer gas, and methane. Two step regeneration tests have been conducted using carbon dioxide as a secondary treatment after a primary reduction

using H_2 , CO, and various combinations of their mixtures. Complete reduction was obtained with H_2 and mixtures of H_2 and CO, but complete sulfur removal was not obtained with CO or methane. It has been found, however, that the reaction rate with CO is faster than with H_2 . When CO_2 was used as a secondary treatment, sulfur removal was increased, particularly for those tests where CO or mixtures of H_2 and CO were used for the primary treatment. Reducing gas utilization has not been clearly established, but some thin bed batch data at a space velocity of 1000 hr^{-1} show about 60% of the reducing gas consumed, and fluid bed data show at least 70% utilization at a space velocity of $37,000 \text{ hr}^{-1}$. Thus, 80-90% utilization of reducing gas might be obtained in a commercial scale regenerator and, in fact, 80% was the value selected for the present designs.

The effect of sorbent sodium concentration on regeneration rate was evaluated over a range of 11-22% sodium. The lower sodium concentration produced a harder sorbent and exhibited higher maximum reaction rates but the overall rates (basis: volume reducing gas consumed per unit time) were about the same in all cases. The effect of increased hardness on attrition rate was not determined. The SO_2 capacity of the sorbents with the lower sodium level was reduced but no data are listed for SO_2 sorption rates.

The regeneration of alkalized alumina has been shown to be highly temperature dependent; e.g., a 1.7 fold increase in reaction rate is realized for each 10°C temperature rise in the temperature range of $650-700^\circ\text{C}$ ($1202-1292^\circ\text{F}$). In addition, most of the experimental data show relatively slow reaction rates at 1200°F and it appears that regeneration temperatures of $1300-1400^\circ\text{F}$ are required if reasonable (i.e., 1-2 hours) holdup times in the regenerator are to be achieved.

All of the presently available experimental data from bench scale and pilot plant measurements of attrition of alkalized alumina indicate unacceptably high rates would be obtained in a commercial unit. A standardized laboratory attrition test unit and method of

reporting results have been developed to facilitate comparison of results from different investigators. The laboratory attrition data are useful for screening purposes and in determining the correlation between sorbent properties (e.g., hardness) and attrition rate, but insufficient data are available to permit prediction of actual plant losses to be made based on laboratory results. Long term steady state data covering a range of operating conditions and sorbents are needed to permit correlation of actual losses with laboratory data.

Based on the results of the data evaluation study summarized above, three different process designs for a commercial size plant have been made for the alkalized alumina process, viz., fixed bed, fluid bed, and dispersed phase. In all three cases the alkalized alumina plant has been sized to treat the flue gas from a 1000 megawatt power plant burning coal with 3% sulfur, and a heat rate of 8600 Btu/kwh has been assumed. These designs were based on available experimental data, supplemented by assumptions where data were missing. The objective in using three different process schemes was to determine which, if any, would be the optimum design considering both economics and operability. Process descriptions and design rationale are presented along with relative merits and approximate economics for the three processes. It should be emphasized that although a suitable sorbent is not presently available, the design economics, and comparisons of the three processes are based on the assumption that a commercially acceptable sorbent will be developed.

The fixed bed process comprises a large number of parallel reactors containing stationary beds of sorbent through which flue gas, heating gas, reducing gas, and cooling gas alternately flow. The main advantages of this process are (1) the sorbent is subjected to substantially less mechanical stress since transfer of the solids between vessels is not required, and (2) the large changes in flue gas flow rates normally encountered do not adversely affect operation.

The main disadvantages are the need for very large (~20' diameter) valves to switch the gas flows between vessels for the different operations (i.e., sorption, heating, etc.), and the potential explosion hazard caused by carrying out the regeneration in the same vessel as sorption, heating, and cooling, thus causing H_2 and CO to come into contact with gases containing small amounts of O_2 at an elevated temperature. The explosion limits of the mixed gases for the design case were calculated based on available literature data but no firm conclusions can be drawn from the results. The literature data required extrapolation and the results were borderline with regard to explosion limits. Therefore, it would be necessary to obtain experimental data for the actual gas composition before building a commercial plant, and if the results show that an explosion hazard exists, an inert gas purge between cycles would be required.

The fluid bed system uses dense phase (30-40 lb/cu ft) fluidized solids reactors and regenerators characterized by moderate gas velocities (2-5 ft/sec) and high solids residence times (1-2 hours or longer if needed). The low gas velocities should help attrition and the long solids residence times permit high sulfur loadings on the sorbent thus minimizing solids circulation rates. Conversely, the low gas velocities require a number of large diameter reactors in parallel (e.g., 10 vessels @ 40 feet diameter) which results in high investment and produces a complicated operation. Since the stability of a fluid bed is dependent upon gas velocity, the reactors and regenerators must be designed such that the lowest actual gas velocity anticipated (e.g., a power plant turndown ratio of about 2), is higher than the minimum fluidization velocity. Under these conditions the entire alkalized alumina plant will run continuously and not require a shutdown of half the system when the power plant output is cut in half which could occur as frequently as once per day.

The dispersed phase design uses a high gas velocity (25-30 ft/sec) and very dilute solids loadings (~0.15 lbs/cu ft). Con-

sequently, only a small number (e.g., 2 @ 40 feet diameter) of reactors are required, but the solids residence time is low and the sulfur loading on the sorbent is correspondingly reduced below that obtained with the other two systems. It is expected that the high gas velocities will cause greater attrition losses than the other two processes but since a suitable sorbent is not presently available, quantitative measurements of these losses cannot be made at this time.

Either a moving or fluid bed regenerator can be used with the dispersed phase reactor. A moving bed design has been used in the present case because calculations show very little difference in cost between a moving and fluid bed, and for this particular design, a moving bed should give better operability. Since the dispersed phase design is dependent on gas velocity, the daily, one half reduction in power plant flue gas flow normally encountered might require a shutdown of one half of the alkalized alumina plant. Consequently, the dispersed phase system has been designed as two parallel trains such that one train can be independently shut down if required. The frequent start-up and shutdown of a moving bed is expected to be much easier than that of a fluid bed, and since the costs are about equal, the moving bed design was selected.

A steam-methane reformer (for producing the reducing gas needed for sorbent regeneration) and a Claus plant (for recovering elemental sulfur from the regenerator off-gas) have been included in each of the three alkalized alumina processes discussed previously. Both of these items are considered to be standard units and it is not expected that either will require development work.

The fixed and fluid bed schemes require a flue gas feed containing as little fly ash as practical since the alkalized alumina beds will act as filters and the sorbent could become deactivated if large quantities of fly ash were added to the system. Therefore, the power plant electrostatic precipitator has been relocated to a position upstream of the air preheater

in the fixed and fluid bed designs. The resulting higher gas temperature in the precipitator increases the gas volume and requires a larger precipitator. The additional cost of the precipitator is considered as part of the alkalized alumina process investment. In the dispersed phase design, the precipitator location is not changed but removal of the SO_2 from the flue gas upstream of the precipitator lowers the collection efficiency and again a larger, more expensive precipitator is required. As before, the additional cost of the precipitator is included as part of the alkalized alumina investment.

The alkalized alumina plants have been designed such that all of the effluent gas (transport air and heater flue gas) is combined with the power plant flue gas for venting from the system. This additional gas is hot so it is admixed with the flue gas upstream of the air preheater. In addition, the hot regenerated sorbent solids raise the flue gas temperature in the reactor such that both the quantity and temperature of the hot gas flowing through the air preheater is increased. Operation of the alkalized alumina process therefore causes an increase in the size and cost of the air preheater and this incremental cost has been included as part of the SO_2 removal plant cost.

Estimates of plant investment for the three process designs were prepared in two parts: part 1, comprising only the sorption-regeneration section, and part 2, the entire plant including the steam-methane reformer, the Claus plant, and the incremental costs of the electrostatic precipitator and air preheater. Originally, Phase 1 results were to be used to select the best process for a prototype plant design as specified for Phase 3 by the contract before it was changed. However, preliminary results from Phases 1 and 2 indicated that more useful information could be obtained by making estimates for complete plants and then determining the effect of various process parameters on economics. Accordingly,

the latter approach will be followed in Phase 3. To provide reasonably sound bases for the estimates, approximate designs of major equipment were made in sufficient detail to insure process and mechanical feasibility, and approximate plant layouts were prepared from which the quantities of large ductwork and piping were determined. With the major equipment specified and approximate plant layouts prepared, standard Kellogg estimating techniques were used to determine the plant investment. The plant location was assumed to be in Ohio, and a labor productivity typical for this area was used in estimating construction man-hours. The accuracy of the present estimates may be considered to be in the range of -5% to +25% based on the current flow sheets and using the techniques described above.

The total annual costs for the three processes have been calculated using capital charges of 13% with other cost items derived from a variety of sources as shown in the main body of this report. There does not appear to be a general agreement as to what the capital charges should be (e.g., TVA suggests 14 1/2%), but for the present evaluations 13% seems to be a reasonable value. Further, NAPCA suggested that for evaluation of area surveys for SO₂ removal capital charges of 13% should be used. The effect of capital charges on process economics will be studied in Phase 3 and, therefore, is not included here.

The investments for the complete plant (i.e., including the regeneration gas producer, the Claus plant, and incremental cost of the power plant electrostatic precipitator and air preheater) have been estimated to be about \$31,000,000, \$36,000,000, and \$40,000,000 for the dispersed phase, fluid bed, and fixed bed designs respectively. Annual costs for the three cases are calculated to be \$7,900,000, \$9,300,000, and \$10,400,000, excluding attrition losses and credit for by-product sulfur. Costs have also been calculated based on assumed attrition rates (0.1% of the solids throughput for the dispersed case, 0.05% for the fluid bed,

and a fixed bed sorbent life twice that in the fluid bed) using a sorbent price of 25 cents per pound and a sulfur credit of \$20 per ton. The results show a net reduction in costs for the fluid and fixed bed cases only. A brief summary of the overall economics is shown below.

	<u>DISPERSED PHASE</u>	<u>FLUID BED</u>	<u>FIXED BED</u>
<u>INVESTMENT:</u> ¹			
Sorption-Regeneration	\$22,100,000	\$27,630,000	\$30,980,000
Complete plant (battery limits)	\$30,720,000	\$35,900,000	\$40,210,000
<u>COSTS</u> ¹ (COMPLETE PLANT)			
<u>\$/YEAR:</u>			
Basic Process ²	7,874,000	9,334,700	10,428,500
Assumed Attrition Loss (@ sorbent cost of 25¢/lb)	926,600	249,400	158,400
Sulfur Credit (@ \$20/ton)	(937,400)	(937,400)	(1,007,400)
Net	7,863,200	8,646,700	9,579,500
<u>\$/TON COAL:</u>			
Basic Process	4.53	5.40	6.01
Net	4.53	4.98	5.52

¹ Alkalized alumina plant sized to treat gases from 1000 MW power plant burning coal with 3% sulfur.

² Excluding Attrition, sulfur credit.

The above costs are based on a load factor (stream efficiency) of 60% (5250 hours per year); i.e., it is assumed that the power plant will operate at full capacity 60% of the time. This is consis-

tent with power plant practice based on a recent survey which showed the largest plants (8.6% of industry) had a 63.6% load factor, a selected group (89% of industry) had 58%, and the entire industry averaged 54%. The effect of load factor on economics will be evaluated in the Phase 3 study whereas only the 60% case is considered here.

The unit costs of 4.53 to 5.52 dollars per ton of coal shown above represent an increase in fuel cost of 70 to 85% based on the 6.50 dollars per ton (25¢/MM Btu) coal used in this study. The relatively minor effect (<10% reduction) of by-product sulfur on overall economics is due to two factors: (1) the low price of sulfur (\$20/ton) that can be expected since it is a by-product, and (2) the small quantities produced (45,000-50,000 tons/year). The cost of sorbent lost to attrition is based on the assumed values listed above but it should be emphasized that to date these low values have not been obtained experimentally; rather, losses of about 7-8% (basis solids throughput) have been observed in the dispersed phase pilot plant. Obviously, the economics shown above are contingent upon the development of a sorbent with much better attrition resistance than exhibited by those that have been tested to date.

A comparison of the above tabulated costs for the three different processes shows the dispersed phase case to have both the lowest investment and operating costs, followed in order by the fluid bed and fixed bed case. It should be noted, however, that if the assumed attrition loss for the dispersed phase case (0.1% of the solids throughput) is doubled, then the total net annual cost becomes about the same as the fluid bed case. Thus it is apparent that the relative economic position of the different cases is very sensitive to attrition loss. Further, the limited data presently available indicate that fixed bed attrition might be small compared to dispersed phase attrition, and therefore, the

assumed differential attrition losses used in the economics evaluation may be too low. When the uncertainties regarding attrition losses are considered, and in light of the sensitivity of process economics to attrition, a firm conclusion as to which of the three processes offers the lowest costs cannot be made at this time.

CONCLUSIONS AND RECOMMENDATIONS

As a result of the data evaluations and process designs reported herein, which are based on information made available to Kellogg under the subject contract, the following conclusions and recommendations are made regarding the alkalized alumina process:

- The process chemistry is technically feasible insofar as the sorbent will satisfactorily remove SO_2 from power plant flue gases and can be regenerated successfully, as demonstrated in bench scale and pilot plant equipment.
- The outstanding technical weakness of the process is the lack of a sorbent that has attrition resistance adequate for commercial operation using fluosolids techniques. Considering the effort that the various organizations (Peter Spence, W. R. Grace, USBM, Kaiser) have spent on sorbent development without producing a candidate with the desired properties, it is possible that the nature of the alkalized alumina/ SO_2 reaction precludes the development of a sorbent suitable for use in a fluosolids system.
- A less attrition resistant sorbent probably would be satisfactory for a fixed bed system if an adequate sorbent life could be obtained (vis-a-vis, chemical activity and/or pressure drop considerations). However, test data on sorbent life and attrition losses in a fixed bed system were not available for this evaluation so conclusions regarding the suitability of the present sorbents for this purpose cannot be made.
- The unexpectedly high costs obtained for the alkalized alumina process coupled with the lack of success in sorbent development led to a reappraisal of the Phase 3 scope as specified in the

present contract, viz., a prototype plant design. Subsequently, Kellogg recommended to NAPCA that a cost sensitivity analysis be substituted for the prototype plant design. It was the basic similarity of all processes for removing SO_2 using a dry sorbent which is chemically regenerated at an elevated temperature that led to this recommendation. Since the SO_2 removal costs, excluding attrition, are largely a function of investment and since any particular process design (hence investment) of the type under consideration is not greatly affected by sorbent properties, it appears that results and conclusions obtained from the alkalized alumina cost sensitivity study will be applicable to processes using other sorbents such as metal oxides. Accordingly, a series of variables to be studied and their ranges was recommended to and accepted by NAPCA as a new phase 3 scope. The phase 3 objective will be to discover which process parameters have the most influence on plant costs thus providing a basis for guiding future research and/or development of dry systems for SO_2 removal. Thus it is anticipated that many of the results obtained in phase 3 will be useful in the preliminary evaluation of other similar processes.

A major finding of the phases 1 and 2 work was the unexpectedly high capital investment required for the alkalized alumina process. The enormous volume of flue gas to be treated combined with its very dilute concentration of sulfur oxides produces unusual process requirements and results in the need for extremely large and costly equipment. A special note should be made of the large lengths of flue gas ductwork required by the alkalized alumina plant. Normally, a power plant is designed such that the gas ductwork is minimized, and the design of the ductwork itself is based on a lower internal pressure than is needed for the alkalized alumina process plants. The combination of high internal pressure (e.g., design value is 45 inches of water for the fluid-bed case) and long runs (hundreds of feet)

results in the gas ductwork becoming a major cost item in the alkalized alumina process plants. Since the volume of gas being handled is nearly a constant, other parameters being equal, it is concluded that ductwork will comprise a major cost item in practically all processes treating flue gases. It is further noted that a sketch of the plant layout, however rough, is essential for estimating ductwork and piping quantities.

- The general economic analysis of the alkalized alumina process, or indeed any SO_2 removal process, involves several factors for which values must be estimated but for which there is no single value that applies in all cases; e.g., load factor (defined as the number of kilowatt hours generated per year as a fraction of the installed generating capacity). Other factors, such as maintenance, must be based on judgment since these are first-of-a-kind plants and direct operating experience is not available. One very important conclusion that has been reached regarding system economics is that credit for by-product sulfur will not offset operating costs and therefore installation of SO_2 removal equipment will always cause an increase in power costs. Based on the above considerations it is concluded that without specific standards (e.g., SO_2 concentration in effluent gas) to guide process design or definite economic goals to meet, and since it presently appears that all of the SO_2 removal processes will cause an increase in power costs, then an economical process is one which causes the smallest increase in power costs. Thus it cannot be ascertained if a process is economical without comparing it to other processes since the economics are on a relative rather than absolute basis. Since many other SO_2 removal schemes are presently being developed, the relative merits of alkalized alumina can be determined only when costs from these other process are available. However, since the alkalized alumina

process increases fuel costs by about 75%, it is concluded that even if a suitable sorbent is developed, it is highly probable that other processes can be developed which will be more economical.

DISCUSSION

A. STATUS OF DATA

1. Attrition

The two major cost items in the alkalized alumina process are capital charges and raw materials, these two comprising about 75% of the total annual cost based on the process economics of Katell (CHEM. ENGR. PROG., 62 (10), 67 (1966)). The sorbent make-up, based on an assumed attrition rate of 0.1% of the sorbent flow to the regenerator, accounts for about 25% of the total cost at an alkalized alumina charge of 25 cents per pound; the balance of raw material costs is due to reducing gas generation. The major contributor to capital charges is the absorber/regenerator combination which accounts for about 17% of the total annual cost. Thus, major criteria for process design should be an absorber/regenerator combination that will give minimum attrition rates and require minimum investment. Since attrition plays a key role in process design and economics, it is important to accurately determine what level of attrition might be expected in a commercial plant. Experimental methods of obtaining attrition data are discussed below.

a. Various Procedures for Generating Attrition Data

Several different types of attrition test units have been used to obtain attrition data. Analysis of the presently available data along with a brief summary of the different attrition test methods is included below. (see Appendix A for details):

(1) USBM Pneumatic Conveyor Attriter

This apparatus consists of a one-inch pipe 28 feet long through which the gas-solids flow, with the gas velocity set at 29 ft/sec; the solids are separated from

the air (in a large diameter chamber) and returned by gravity flow to the attriter inlet. Attrition rate is reported as the amount of fines (size not defined) collected in 24 hours as a percentage of total weight of solids circulated in that period. After 10 days of operation (19 cycles/hour or about 4500 cycles total), the attrition rate was 0.005% and the particle size had decreased slightly, i.e., from 82% 8-10 mesh and 18% 10-12 mesh initially to 46% 8-10 mesh and 40% 10-12 mesh after 10 days. By converting these data to a basis of inventory, rather than circulating solids rate, the attrition loss becomes 2.28%.

(2) Tyler Sieve Shakers

Tyler "Ro-Tap" testing sieve shakers were used to test Grace No. 1 (standard) alkalized alumina in various physical forms (as received, after 600°C and 122°C air roast, after 600°C H₂ roast), and two different catalyst supports. Attrition loss is defined as the percent reduced to minus 60 mesh. Results of these tests show that increasing the hardness (crushing strength) of the material does not necessarily increase attrition resistance.

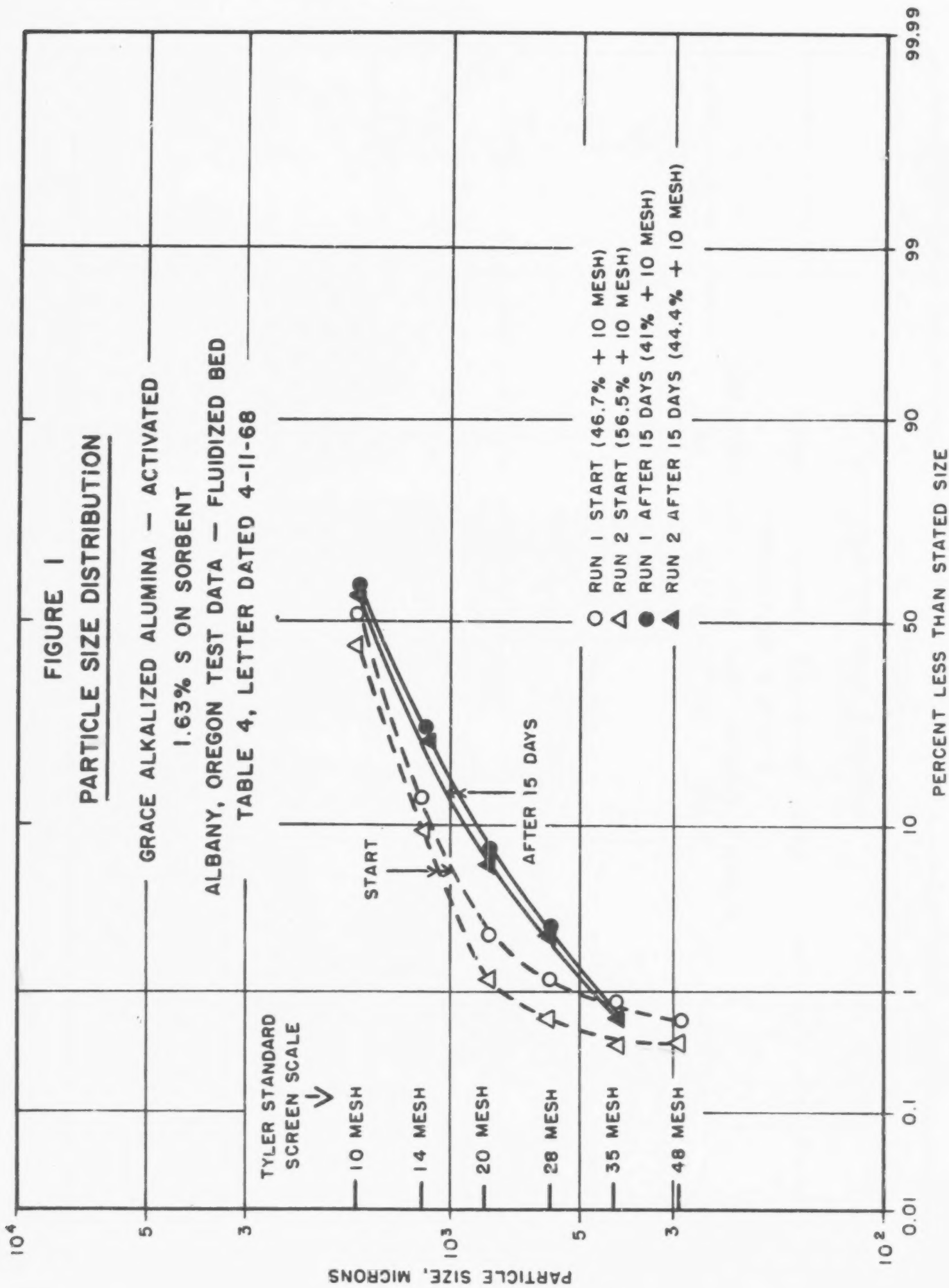
(3) USBM - Albany - Fluid Bed and Air Lift
Attrition Test Unit

USBM at Albany Metallurgy Research Center has developed both a fluidized-bed and an air-lift attrition test unit. Reported gas velocity is 1.8 feet/sec in the fluid-bed and about 25 feet/sec in the air lift. Attrition loss is measured as the weight loss per 24 hours (reported as percent of inventory per hour) with daily additions of material to maintain the original sample weight (50 and 10 grams for the fluid and air lift units respectively). Size distribution at the start and after 15 days are reported along with the daily and total weight loss. Grace #1 absorbent with various levels of sulfur was tested.

The fluid bed size distribution data for the activated (1.63%S) and a loaded (8.85%S) sample have been plotted on logarithmic probability paper, Figures 1 and 2. As is evident from these plots, there is essentially no increase in the quantity of fines which is not too surprising since the method of testing eliminates the fines from the system. After 15 days the particle size distribution has been shifted slightly such that a more even distribution of the various fractions is obtained; i.e., the quantity of minus 10 plus 35 mesh material has been increased. By inspection the other samples show the same characteristics and therefore have not been plotted. This slight decrease in particle size should help rather than hurt absorption rates since an increase in surface area is obtained.

The attrition rates obtained in the fluid-bed unit decrease rapidly the first few days and then level out to essentially constant values after about 7-10 days; also they generally show decreasing values with increasing sulfur content (may be due to increasing density) as illustrated by the data (Grace #1 absorbent) in Table 1.

The data in Table 1 indicate that regeneration apparently weakens the absorbent and causes the attrition rate to increase. These data are based on only one loading and regeneration but verbal information from Albany indicates essentially no change after 10 cycles. While these data probably cannot be used directly as design data, they are useful for screening purposes and when compared to the air-lift data could give an indication of the relative attrition rates of the two systems if a common basis of comparison can be found. Listed in Table 2 are data for the two systems for Grace #1 absorbent; note that comparisons have been made on three different bases-- the rates for the 1st 3 days, the rates for the 3rd day, and the air-lift 3rd day rate with the last 5 days for the fluid-bed rate.



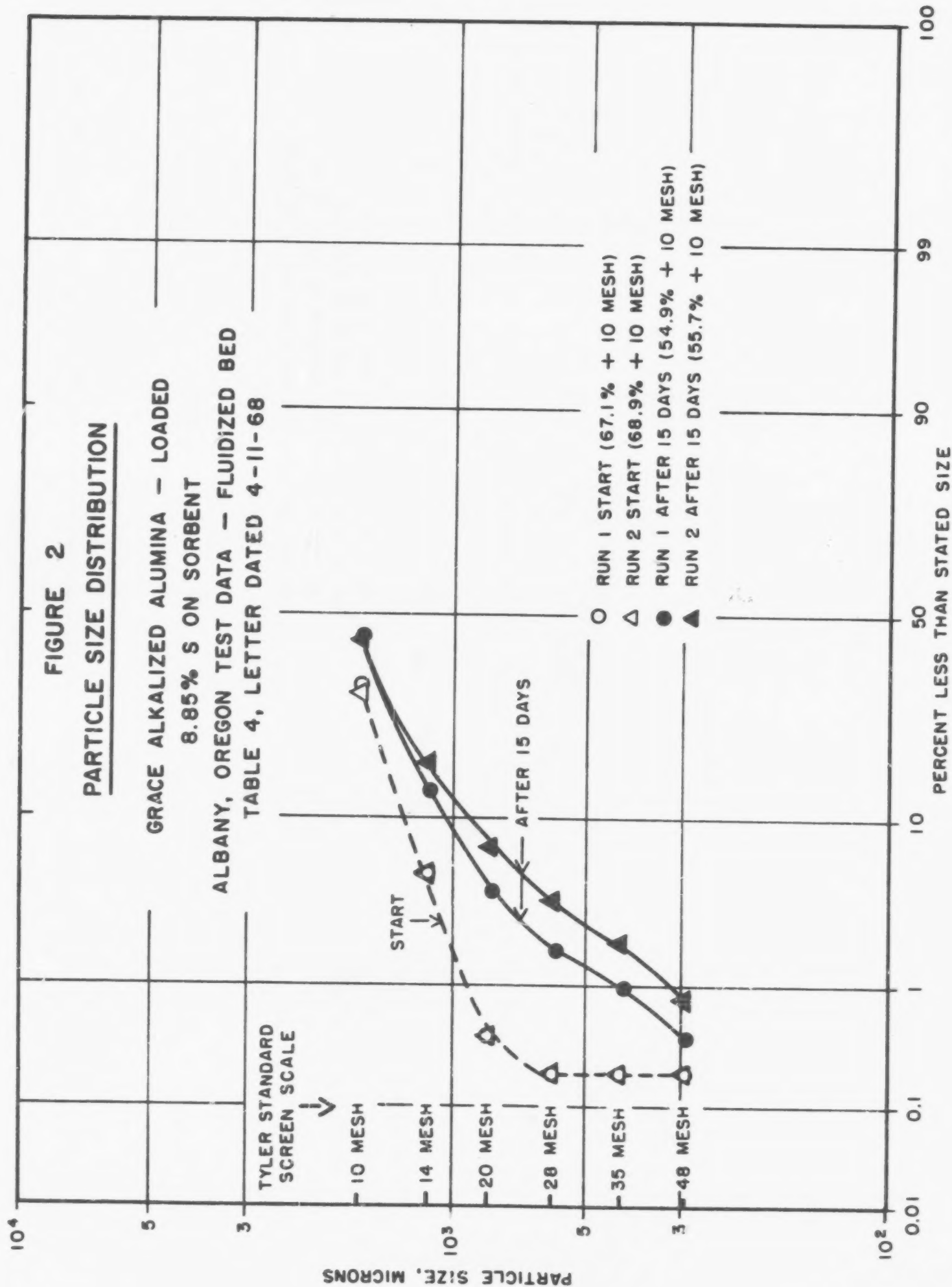


TABLE 1

FLUID BED ATTRITION TEST UNIT DATA

<u>SAMPLE</u>	<u>% S</u>	<u>AVERAGE ATTRITION LOSS*, % OF INVENTORY/HR</u>		
		<u>1ST 5 DAYS</u>	<u>2ND 5 DAYS</u>	<u>3RD 5 DAYS</u>
Activated	1.63	0.151	0.078	0.064
Loaded	2.29	0.180	0.092	0.078
Loaded	5.87	0.106	0.068	0.063
Loaded	8.85	0.037	0.036	0.030
Regenerated	1.38	0.279	0.163	0.144

* USBM-Albany - April 1968 Monthly Summary

TABLE 2

**COMPARISON OF SORBENT ATTRITION LOSSES FOR AIRLIFT
AND FLUID BED SYSTEMS**

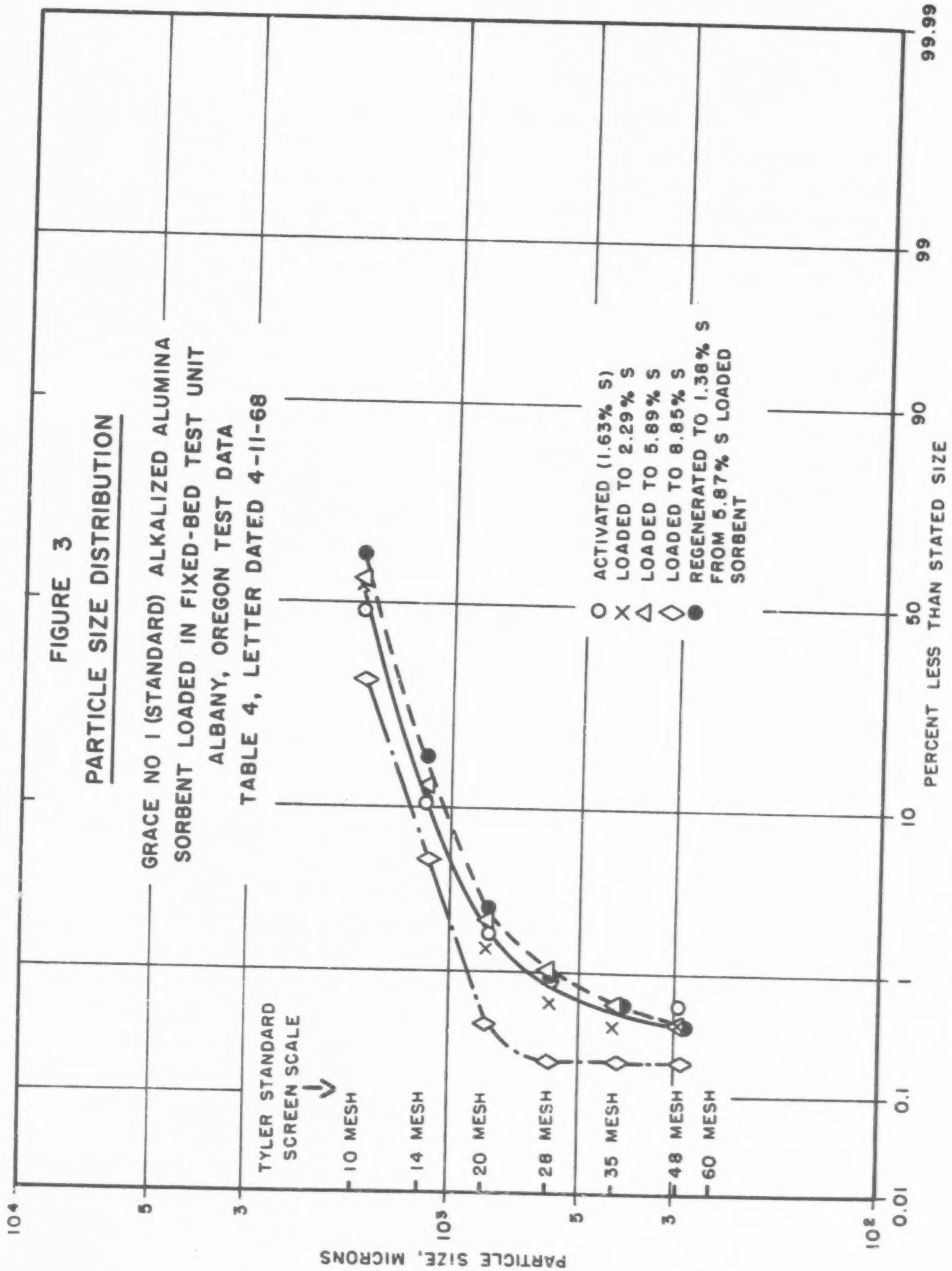
<u>SAMPLE</u>	<u>%S</u>	<u>ATTRITION LOSS*, % OF INVENTORY/HOUR</u>				
		<u>AIR LIFT</u>		<u>FLUID-BED</u>		
		<u>1ST 3 DAYS</u>	<u>3RD DAY</u>	<u>1ST 3 DAYS</u>	<u>3RD DAY</u>	<u>LAST 5</u>
Activated	1.63	1.29	1.33	0.19	0.13	0.064
Loaded	8.85	0.79	0.52	0.04	0.05	0.030
Regenerated	1.38	2.70	2.52	0.33	0.24	0.144

<u>SAMPLE</u>	<u>%S</u>	<u>RATIO: AIR-LIFT/FLUID-BED</u>		
		<u>1ST 3 DAYS</u>	<u>3RD DAY</u>	<u>3RD DAY/LAST 5</u>
Activated	1.63	6.8	10.2	20.8
Loaded	8.85	19.8	10.4	17.3
Regenerated	1.38	8.2	10.5	17.5

*USBM-Albany-April 1968 Monthly Report

The comparison of the rates for the first 3 days show more variation than do the other comparisons, possibly because of varying amounts of fines initially present in the different samples. The 3rd day rates are quite consistent but the fluid bed test probably had not reached steady state conditions, except perhaps for the loaded sample. Thus the most valid comparison probably is the one between the air-lift 3rd day rate and the last 5 days rate for the fluid-bed since these data are the ones most likely to be for steady state conditions. A direct comparison shows the air-lift rate to be about 10-20 times the fluid bed rate but this may not be a valid comparison. Since the air-lift test conditions are such that apparently the inventory is cycled about 6400 times per day (see section 5. C. (1) below), the equivalent time in a commercial unit that this represents compared to the equivalent time of the fluid bed is needed.

The size distribution of Grace #1 sorbent with various levels of sulfur are reported in the Albany attrition test results discussed above. The samples were loaded using a synthetic flue gas and regenerated in a fixed bed test unit and any attrition produced during these tests would therefore be due to chemical rather than physical action. The data have been plotted (Figure 3) in the usual way and the results show that there was no increase in the minus 60 mesh material for any of the samples, and in fact, an increase in particle size was obtained for the 8.85%S item. There appears to be a small increase in the plus 48 minus 10 mesh fraction for the regenerated sample but the change is small. Based on these data it is concluded that the attrition exhibited in the Albany test units using a synthetic flue gas is due to physical rather than chemical action, per se. However, it is quite possible, and indeed, quite likely, that the chemical changes create stress in the particles and weakens them such that subsequent physical actions results in high attrition rates.



(4) W. R. Grace Accelerated Air Jet Attrition
Test Unit

W. R. Grace and Company developed a new attrition test for testing alkalized alumina sorbent, viz., the accelerated air jet attrition test (AAJA). Basically it comprises blowing air through the sample for a specified time, and then weighing the material retained on a 14 mesh screen. Attrition loss is reported as weight percent loss determined by difference between the original and final sample.

Some values have been reported by Grace for both Grace #1 (standard) and #2 (improved) but other than for comparative purposes (#2 worse than #1), these data presently have little practical use. To date, the generally accepted definition of fines for this process is minus 60 mesh material and since the Grace test reports all minus 14 mesh as fines, meaningful comparisons with other data are essentially impossible without knowing the percent of -60 mesh material in the 14 mesh fraction. Also, comparisons of results of different materials tested on the Grace unit may be masked by the large size screen used, in that two materials showing the same loss could have quite different size distributions. For example, a material with a 50% minus 14 mesh could also have 50% minus 60 mesh while another sample with 50% minus 14 mesh might have 0% minus 60 mesh. These limitations severely limit the usefulness of the Grace attrition data and modifications either to the test procedure, or methods of reporting data are indicated.

(5) Standard of Indiana-Cracking Catalyst Test
Procedure

A description of the attrition test method generally used for determining relative attrition rates of cracking catalysts is included in Appendix A; two variations are shown, the

forty-five hour and the one-hour methods. The one-hour method is basically the one developed by Standard Oil Company (Indiana) and published in IEC, 41, 1200 (1949). The test does not require elaborate equipment, is easy to run, and the results are reported in terms of an attrition index or attrition rate which permits a rapid, direct comparison of the attrition resistance of different catalysts.

Possibly this test could be used for testing the alkalized alumina sorbent but since it has much larger particles than cracking catalysts, modification of the equipment and/or procedure may be required to obtain good fluidization with the heavier particles (e.g., a larger size orifice may be needed). However, any modification required probably could be determined with 2-3 tests and the modified test procedure could then be used by all the various investigators working on development of the alkalized alumina. The attrition index of the standard (Grace #1) sorbent could then be determined and used as the reference point since some pilot plant attrition data are available for this material. The attrition rate of the standard appears to be unacceptably high so an improved sorbent would have to exhibit a lower attrition index to warrant further testing. A modified Standard of Indiana attrition test was later developed by Kellogg and recommended for general use (see section 1-d below).

b. Distribution of Attrition Losses

A one-cycle attrition test was run in the Bruceton pilot plant in an attempt to determine where the attrition occurs. The pilot plant was cleaned of sorbent and about 1500 pounds of loaded, test sorbent charged to the regenerator; this sorbent had previously been through about 9-10 absorption, regeneration cycles and the size distribution was determined prior to charging. The sorbent was regenerated for 10 hours

with steam reformed methane, drained, the size distribution determined, returned to the system, and pneumatically conveyed to the top of the reactor. The size distribution of the conveyed material was then determined, next, sorption was carried out in the usual manner at a feed rate of 180-190 lb/hr so the test took some 8 hours. After completion of the sorption run, the system was drained (essentially a 100% weight balance was obtained) and size distribution determined on each stream; i.e., the bottom discharge, the recycle and the overhead. These data have been plotted in the usual manner (Figures 4 and 5) and the attrition loss calculated for each step. Attrition loss is defined as the percent increase of minus 60 mesh fines compared to the original material. A summary of these data is shown in Table 3.

TABLE 3
DISTRIBUTION OF ATTRITION LOSSES

	%-60 Mesh	Increase in -60 Mesh	Attrition Rate*	% of Total
After Regeneration	2.65	1.44	1.46	21.4
After Conveying	3.06	0.41	0.42	6.2
After Sorption	7.94	4.88	4.94	72.4
Total	-	6.73	6.82	100.0

* Attrition rate = $\frac{(\text{increase in } -60 \text{ mesh})}{(100-1.21)} \times 100$

Note: Original sample contained 1.21%-60 mesh.

It is quite obvious from the Table 3 values and from Figure 4 that sorption causes most of the attrition while conveying causes very little. It is also apparent that the total loss of 6.82% is unacceptable high. The regeneration attrition rate may not be a true value because of the method of filling the regenerator, i.e., the sorbent was fed into the top in a

FIGURE 4

CHANGE IN PARTICLE SIZE DURING ABSORPTION-REGENERATION CYCLE

BUREAU OF MINES, PITTSBURGH COAL RESEARCH CENTER DATA

TABLE 4, BM-19, QUARTER ENDING 12-31-67

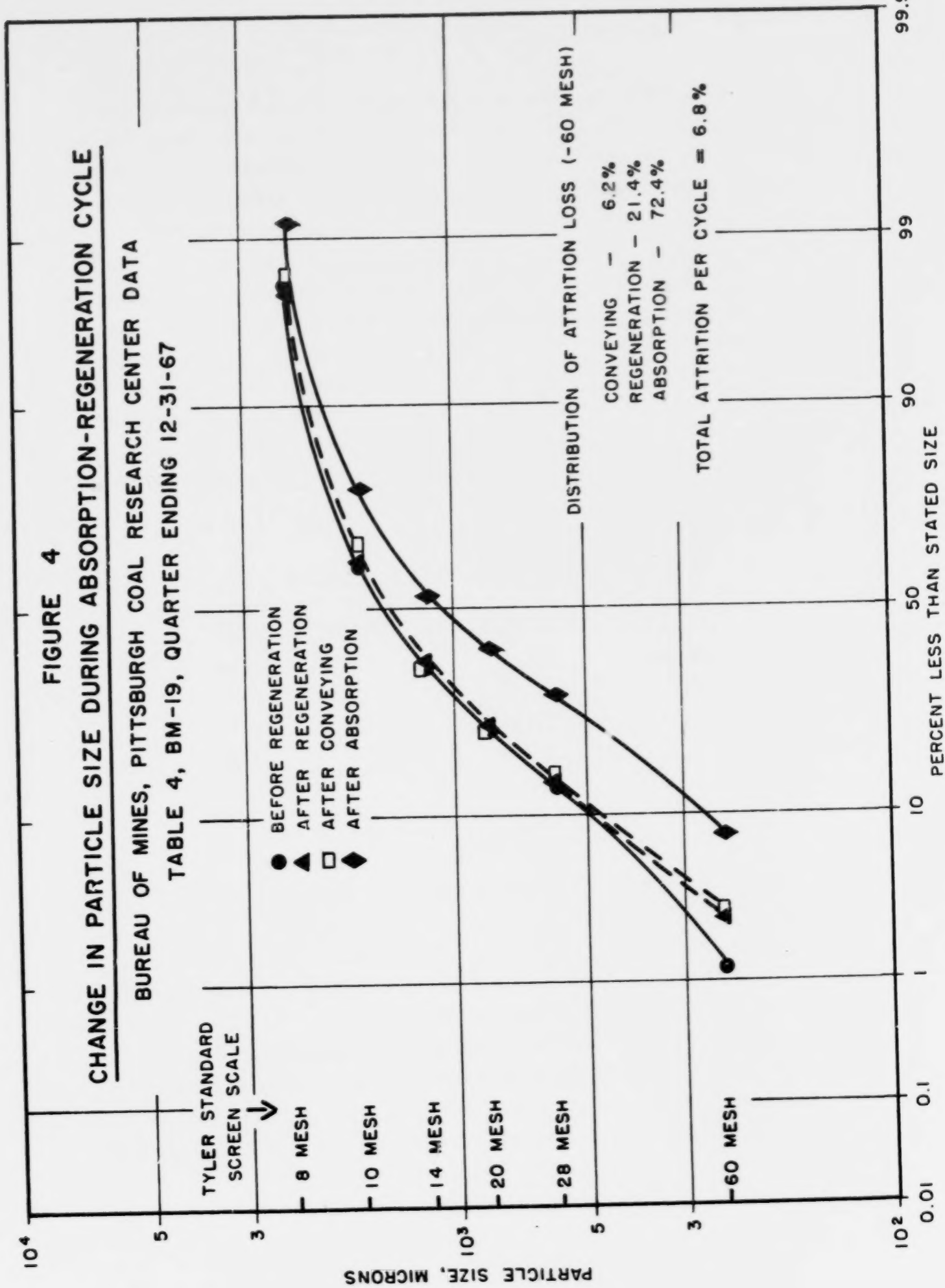
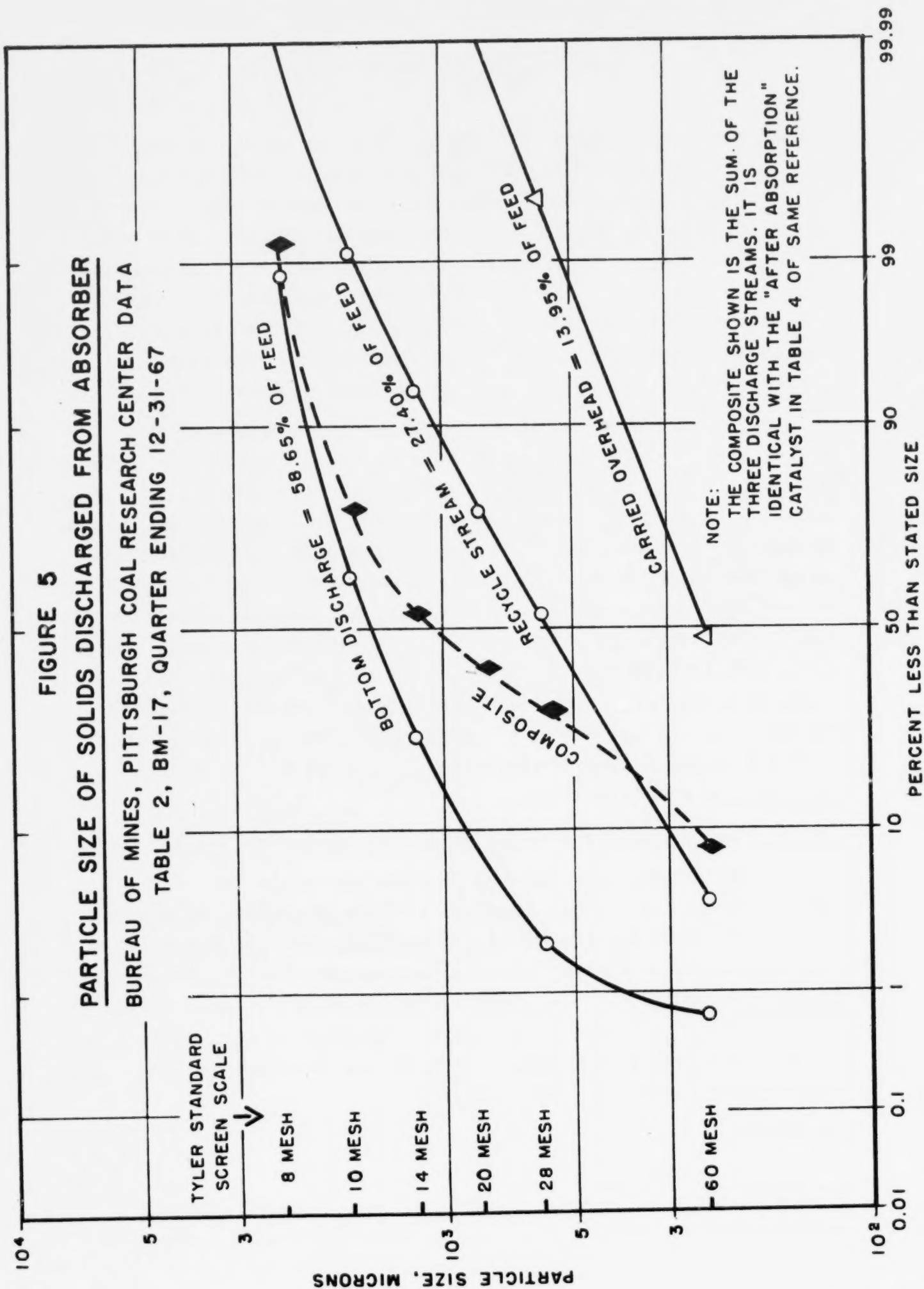


FIGURE 5
PARTICLE SIZE OF SOLIDS DISCHARGED FROM ABSORBER
 BUREAU OF MINES, PITTSBURGH COAL RESEARCH CENTER DATA
 TABLE 2, BM-17, QUARTER ENDING 12-31-67



normal manner but since the regenerator was initially empty, the particles' free fall distance was greater than with a full vessel. Consequently, the force of impact was greater which could cause higher attrition values. On the other hand, a fixed bed rather than a moving bed was used for the regeneration step and this would tend to cause lower attrition rates. The relative effect of these two factors (greater free fall distance, fixed bed) on the regeneration attrition rate is unknown and the Table 3 values therefore may be misleading.

It should be noted that the bottoms product comprises almost 60% of the fresh feed (Figure 5) which results in a low residence time for the largest particles, thus causing low sulfur pickup by this fraction. Recycle of this bottoms stream, rather than the overhead, would permit higher sulfur loadings to be obtained and could possibly reduce attrition losses; i.e., larger particles would be recycled and as these attrite they would leave with the overhead stream to the regenerator. Thus the particle size distribution should become narrower and a lower slip velocity could be used, thereby providing larger contact time in the reactor. Pilot plant tests using recycle of the bottoms stream could determine the effect on sulfur loading and attrition loss.

c. Comparison of Experimental Data on Common Basis

An attempt was made to compare the Albany air-lift attrition data with that reported for the Bruceton pneumatic conveying test loop discussed previously. The pneumatic conveying results are reported as a percentage of circulating solids whereas the Albany data are shown as a percentage loss of inventory. Therefore, a direct comparison cannot be made but with certain assumptions the data can be converted and compared on a similar basis.

(1) Albany Data Converted to Circulating Solids
Basis

Basis:

- solids density in the air-lift tube of 0.15 lb/ft³, assumed based on pilot plant data for similar operating conditions.
- average solids velocity through the air-lift tube of 2 ft/sec, estimated based on particle settling velocity and gas velocity.
- tube diameter is 1" and length of air-lift tube is 12", based on sketch of equipment
- at 2 ft/sec and 1 ft tube length, time per pass is 0.5 sec.
- sorbent inventory is 10 grams

$$\text{Tube Volume} = (\pi/4) (1/12)^2 (1) = 0.00545 \text{ ft}^3$$

$$\begin{aligned} \text{Circulating rate} &= \frac{0.00545 \text{ ft}^3 (0.15 \text{ lbs/ft}^3) (24 \text{ hrs/day})}{0.5 \text{ sec (1 hr/3600 sec)}} \\ &= 141.26 \text{ lbs/day} \end{aligned}$$

$$\text{and } \frac{(454 \text{ gms/lb}) (141.26 \text{ lbs/day})}{10 \text{ gms inventory}} = 6400 \text{ cycles/day}$$

Albany 3rd day air-lift data (April 1968 Monthly Report) show 3.2 grams average weight loss/day for Grace #1 activated absorbent.

∴ Attrition based on solids circulating rate =

$$\frac{3.2 \text{ gms/day (100)}}{(454 \text{ gms/lb}) (141.26 \text{ lbs/day})} = 0.005\%$$

This rate is in good agreement with the Bruceton pneumatic conveying 2-4 day rate of 0.006% and the 10th day rate of 0.005%.

It should be kept in mind that the conversion of the Albany data to a different basis is based on assumptions

as to average particle velocity and solids density in the air-lift tube. Bases for these assumptions were solids densities reported for the Bruceton pilot plant, and calculated settling velocities of 14 mesh particles. Thus, the assumptions should be reasonably accurate. It should also be kept in mind that different sorbents were tested in the two units: the standard (Grace #1) sorbent in the Albany unit, but the source of the conveying test sorbent is not clearly stated.

One other important point to be noted in comparing the Albany air-lift and Bruceton pneumatic conveying test loop data is that the air-lift tube is only one foot long whereas the Bruceton unit is 28 feet in length. The close agreement of the results when the difference in lengths is neglected, as was done in the above calculation, indicates that either 1) the assumptions are wrong, 2) the end effects (i.e., solids pickup and disengagement) cause most of the attrition, or that 3) the two sorbents tested have different properties which offset the difference in apparatus. It is possible that for the lengths of pipe tested, the attrition in the pipes themselves is small compared to that resulting from entraining and disengaging the solids. In this latter case the attrition would be essentially independent of length but would vary directly with the number of cycles to which the sorbent is subjected. In any event, the results show the need for reporting data on a common basis if meaningful comparisons are to be made.

(2) Bruceton Data Converted to Inventory Basis

The data described in (1) above can also be converted to an inventory basis and this has been done as shown below. Assumptions are the same as those previously used.

Bruceton Inventory - 19 passes/hr or hourly
circulating rate was 19
x inventory.

Reported attrition loss = 0.006% of 24 hr
circulating rate

$$\therefore \text{Conversion to inventory} = 0.006(19)(24) = 2.74\%$$

This is quite different from the 32% value obtained with the air-lift. It should be noted, however, that the air-lift inventory of 10 grams was cycled 267 times per hour (based on the calculations in the previous section) compared to 19 passes per hour for the Bruceton inventory. Thus, adjusting for the number of times the inventory is circulated through the equipment, the Bruceton loss becomes:

$$(267/19)(2.74) = 38.5\%$$

This rate is in good agreement with the 32% obtained in the Albany unit.

d. Recommended Method of Attrition Testing

It has been previously pointed out (section 1-a-(5) above) that the various laboratory attrition tests presently used by the different investigators need to be standardized to facilitate comparison of data from different sources. Further, modifications of the tests themselves would probably give more meaningful results. Consequently, MWK undertook the task of modifying the Standard of Indiana attrition test so that it could be used for testing the alkalized alumina sorbent. One sample each of Grace #2 and a Peter Spence sorbent was obtained from Bruceton and used for the test work. Concurrently, AVCO ran a similar Grace #2 sample on a modified AAJA test apparatus.

The MWK modified Standard of Indiana test uses a 3/64 inch diameter orifice instead of the standard 0.0150 inch diameter and the orifice pressure drop is lowered to

20 psi (vs. 55-60 psi standard). The length of the test remains at one hour. The AVCO modified AAJA test increases the opening of the flask to 3-1/2 inches and uses a 60 mesh (U.S.) screen instead of a 14 mesh screen. Second degree of severity conditions are used. Results of the AVCO test were obtained from NAPCA for comparison with the MWK results.

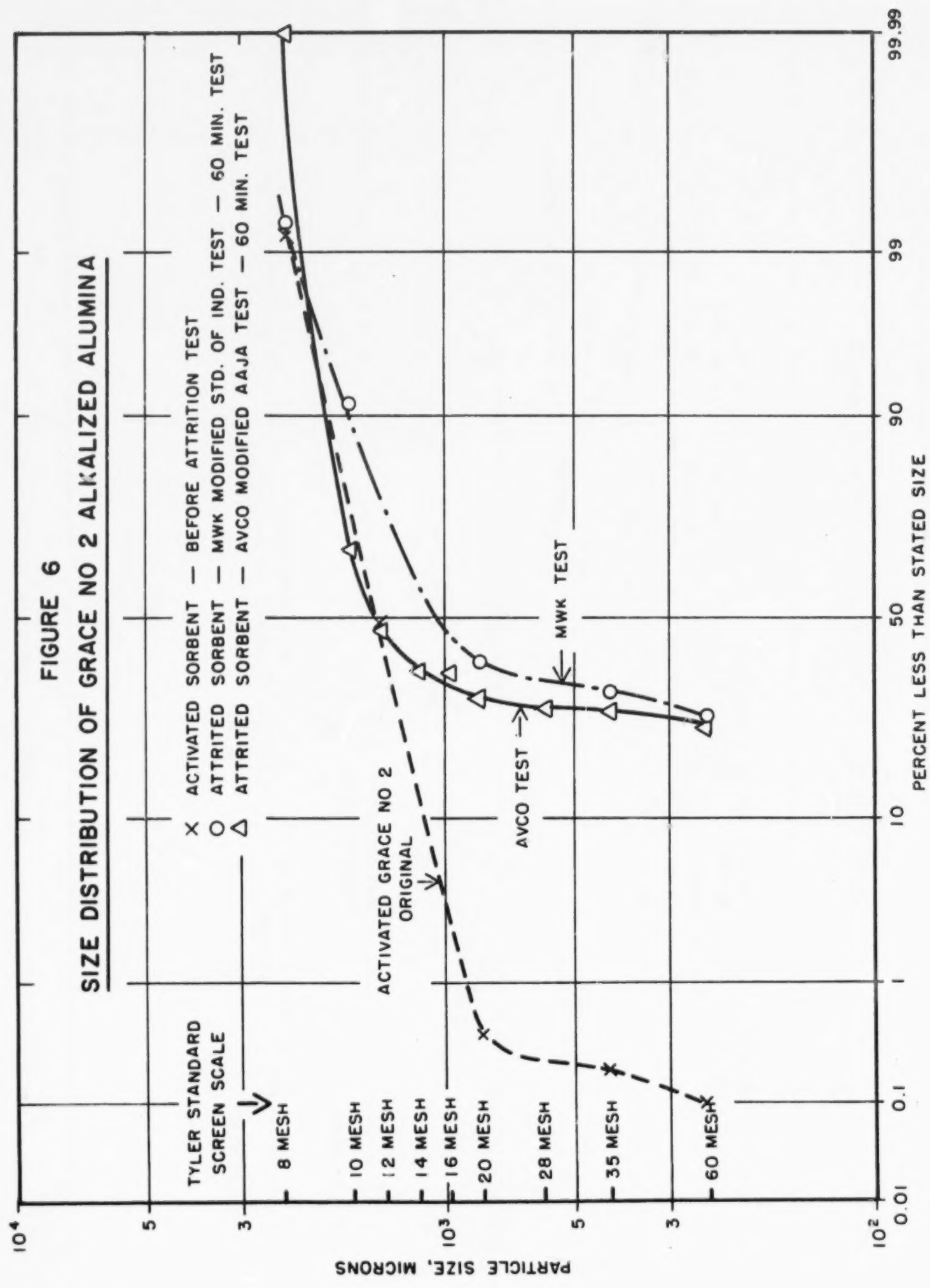
The size distribution curves of the original and attrited sorbent for both the MWK and AVCO tests are shown in Figure 6. These same curves are also shown in Figure 7 along with the corresponding curves for the Peter Spence sorbent. Prior to testing all MWK test samples had been activated with H₂ for 10 hours at 630°C compared to 10 hours at 650°C for the AVCO sample; therefore, the starting material for both the MWK and AVCO tests is essentially the same.

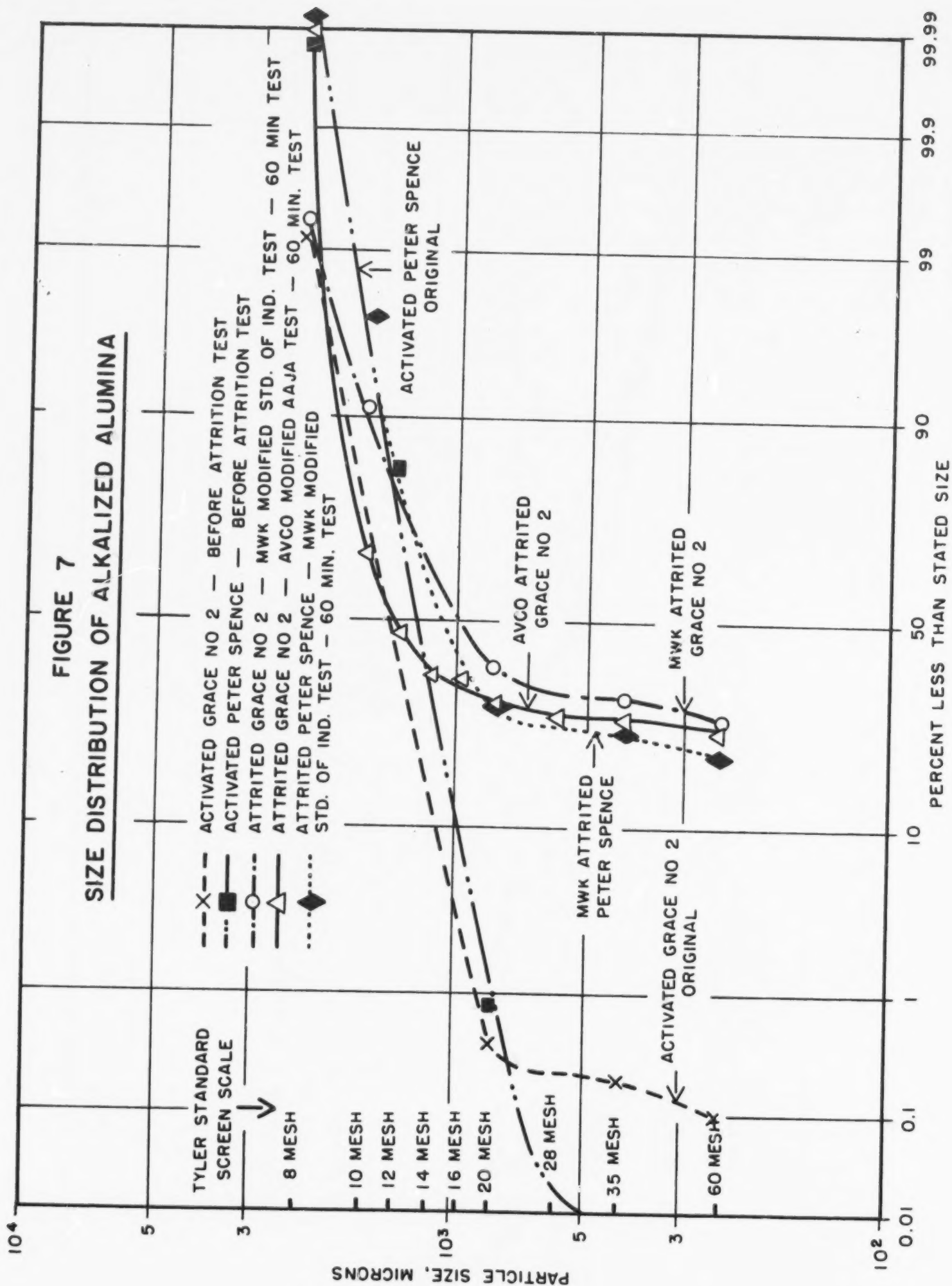
Examination of the plots shows that in all cases the attrited material has about the same size distribution as the original material down to about 14-18 mesh (U. S. Sieve Series), but at this point the particle size of the attrited material decreases rapidly. The actual quantities of fines (-60 mesh) produced during the tests are:

AVCO test on Grace #2	-	25.7%
MWK test on Grace #2	-	26.7%
MWK test on Peter Spence	-	21.1%

Thus, the results indicate that both the AVCO modified AAJA and the MWK modified Standard of Indiana tests give equivalent attrition losses on Grace #2. The MWK test on Peter Spence material produced about 20% less fines than on the Grace #2, but more data are required to determine if this difference is significant. Further information is required on reproducibility of both sorbents add test procedures as well as correlation of test data with pilot plant data, but for screening studies, the modified test appears to be superior to the methods previously

FIGURE 6
SIZE DISTRIBUTION OF GRACE NO 2 ALKALIZED ALUMINA





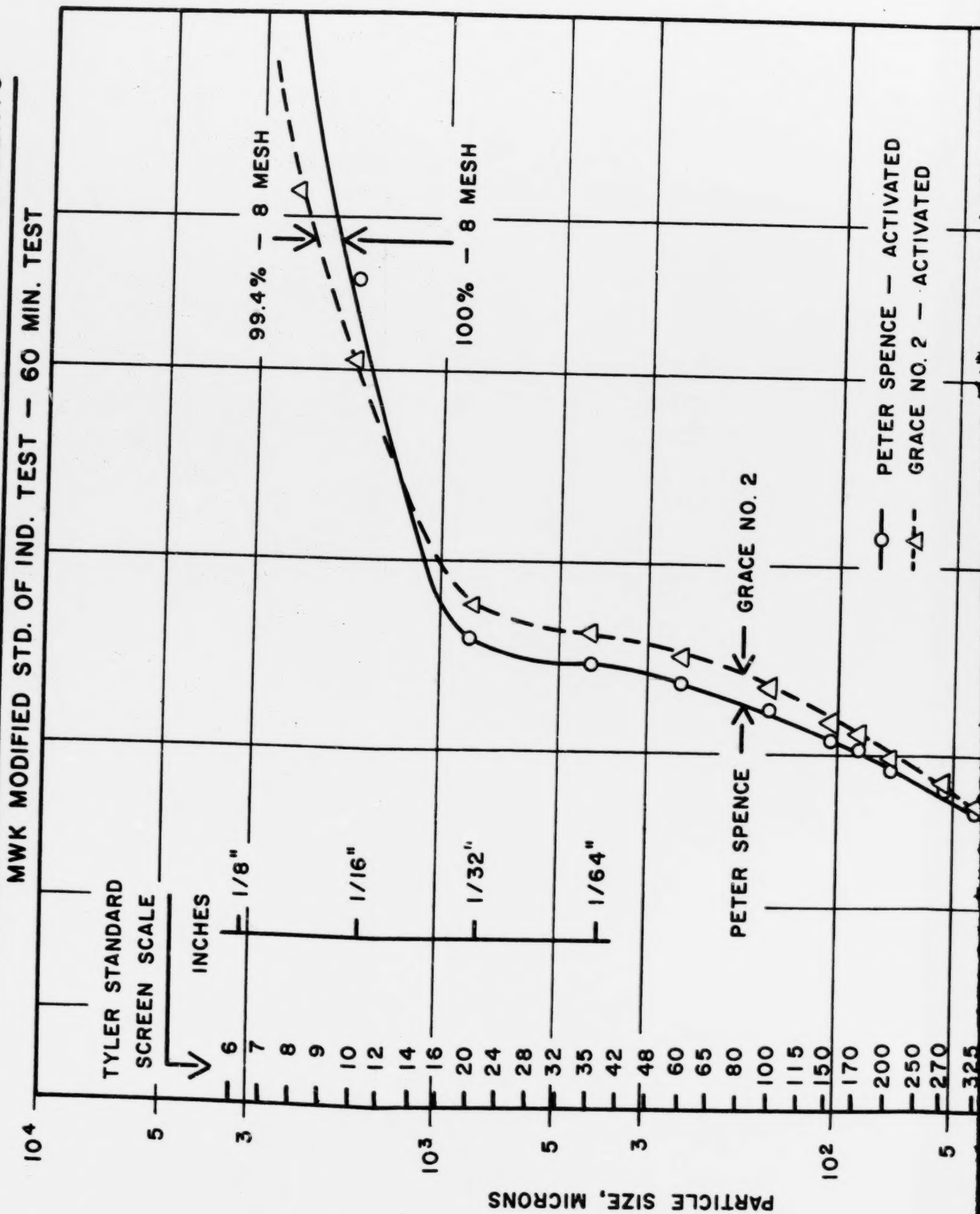
used. Subsequent to these tests, the AVCO modified AAJA test was adopted as the standard test.

The necessity of obtaining a particle size distribution of the attrited material is illustrated by Figures 6 and 7. For all three materials tested, the curves drop off sharply below about 14-18 mesh, as previously noted, but the -16 mesh fraction is still higher than the -60 mesh fraction; e.g., 38% vs. 26.7% in the AVCO test. Note that mesh sizes referred to are U. S. Sieve Series. Thus reporting only the -16 mesh material, as is presently done, would indicate significantly higher losses than obtained based on -60 mesh material. If the attrition characteristics of the sorbent were such that a flatter curve were obtained, the difference in the -16 and -60 mesh fractions would be greater. In fact, the shape of the particle size distribution curve might be used as a guideline in sorbent development work; i.e., the desirable properties or processing conditions would be those that tend to produce a size distribution curve with a flat slope.

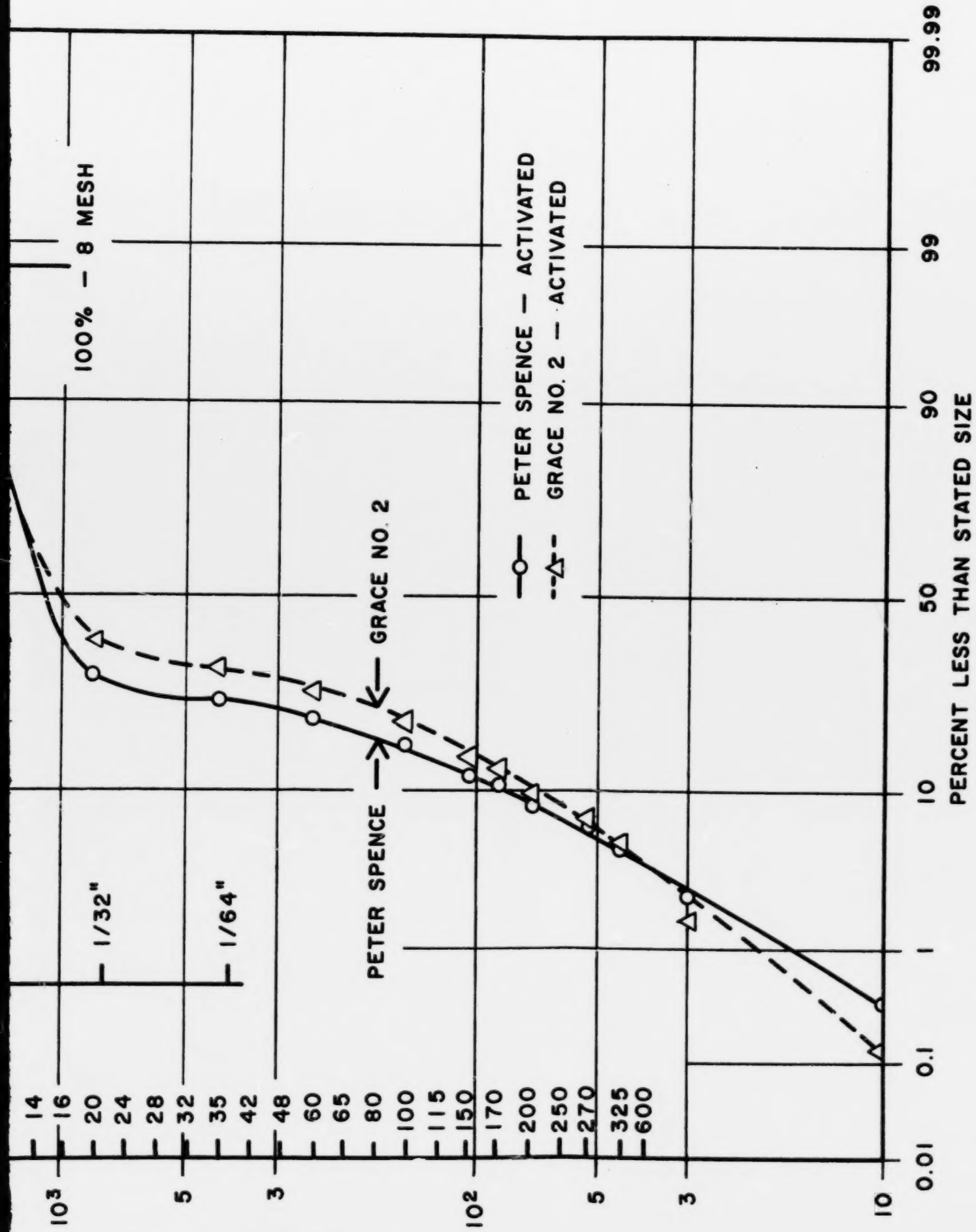
Visual observation of the attrited material revealed that the -60 mesh fraction produced in the test was actually much smaller than 60 mesh, so a particle size distribution was obtained on the MWK attrited -60 mesh material and the complete distribution curve is shown as Figure 8. The above two observations, viz., 1) fines much smaller than 60 mesh, and 2) above about 16 mesh the attrited and original material are essentially the same, lead to the conclusion that most of the fines produced come from some particles that completely disintegrate while other particles remain essentially unchanged. Thus, it would seem that the sorbent might be a mixture of particles with significantly different physical properties. Therefore, a 2-stage attrition test is indicated to determine if the present sorbents are indeed mixtures of particles having attrition resistance ranging

FIGURE 8

SIZE DISTRIBUTION OF LABORATORY ATTRITED SORBENTS



PARTICLE SIZE, MICRONS



from very poor to very good. The 2-stage test would comprise running a standard attrition test, screening the attrited material, and re-running the standard attrition test on the coarser fraction, say + 16 mesh material. If the attrition loss from the second test is lower than from the first test, it would indicate a significant difference in physical properties among the different particles. In this case, the sorbent manufacturing process could be revised whereby an attrition step with fines recycle is included to produce a more attrition resistant material as the final product. Alternatively, the commercial plant could be designed such that standard cyclones would recover the fines (normally 100% recovery down to about 40 microns is obtained) which could be re-balled and recycled back to the alkalized alumina plant.

e. Methods to Improve Attrition Resistance of Alkalized Alumina

Pilot plant evaluation of commercial sorbents subjected to several cycles of intermittent operation--sorption followed by regeneration--and also subjected to continuous pilot plant operation indicated that attrition losses were greater than acceptable for plant operation. Physical strength decreased during activation and operating techniques to significantly reduce physical degradation were not found. Consequently development programs were initiated for the purpose of finding a method of preparing an attrition resistant sorbent which still retained its high activity.

(1) Prediction of Pilot Plant Performance from Laboratory Testing

Since poor performance of the sorbents used in the pilot plant had prevented correlation of laboratory attrition test results with steady-state plant losses, it was decided to

operate the pilot plant using a highly attrition resistant inert catalyst support. The support, 1/16-inch diameter porous alumina spheres, was purchased from Universal Oil Products Corporation. Since SO_2 was not being sorbed, air rather than reformed natural gas passed through the regenerator and the regeneration level was controlled to give three hours residence time. Attrition loss was determined by periodically discharging and weighing the solids. At each draining a representative sample was collected and material was added to restore the original inventory.

Pilot plant operation was terminated after 95 sorption-regeneration recycles. Attrition loss averaged 0.12% of inventory per cycle. USBM states that part of the loss was due to operation of blast gate valves below the sorber and regenerator. Particle size distribution, Figure 9, indicates that steady-state had been reached after about 44 cycles.

In previous pilot plant experiments attrition loss was measured for Kaiser No. 1 and Grace No. 2 sorbents. Even though steady-state values were not obtained, the initial measurements were made at operating conditions comparable to those used with the inert support. At these conditions, Grace sorbent attrited at 1.8% per cycle and the Kaiser sorbent at 2.3% per cycle. Attrition resistance of retained samples of these sorbents and of the inert support were measured in the laboratory using USBM and NAPCA accelerated air jet procedures. It should be noted that the NAPCA test is the AVCO modified AAJA test previously described while the USBM tests represents a further modification to permit the use of a smaller sample. A comparison of these two methods is shown in Figure 10. The relationship of USBM and NAPCA laboratory-attrition loss with pilot plant loss at approximately similar operating conditions

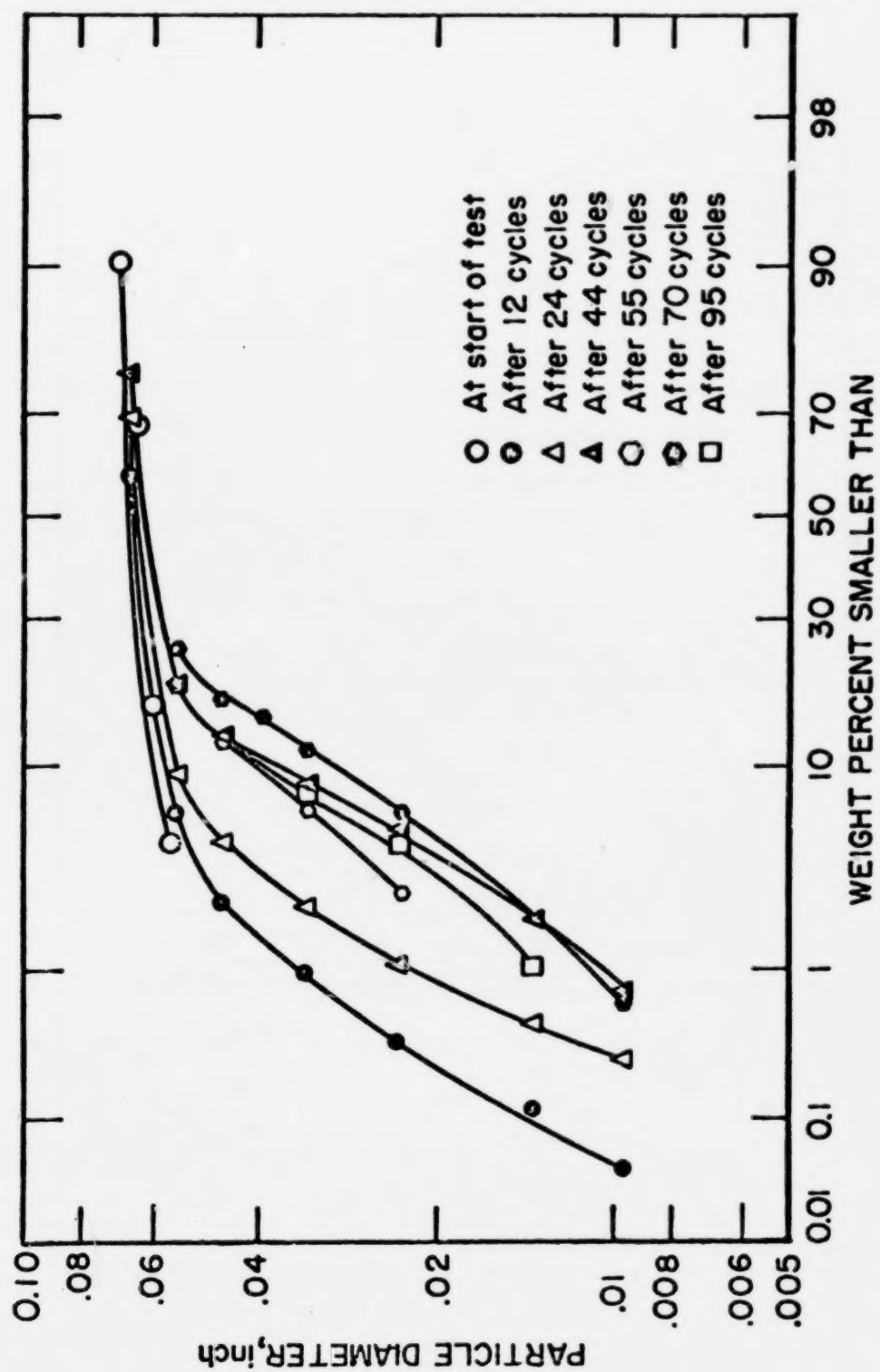


Figure 9--Particle size distribution during pilot plant operation using a spherical alumina catalyst support.

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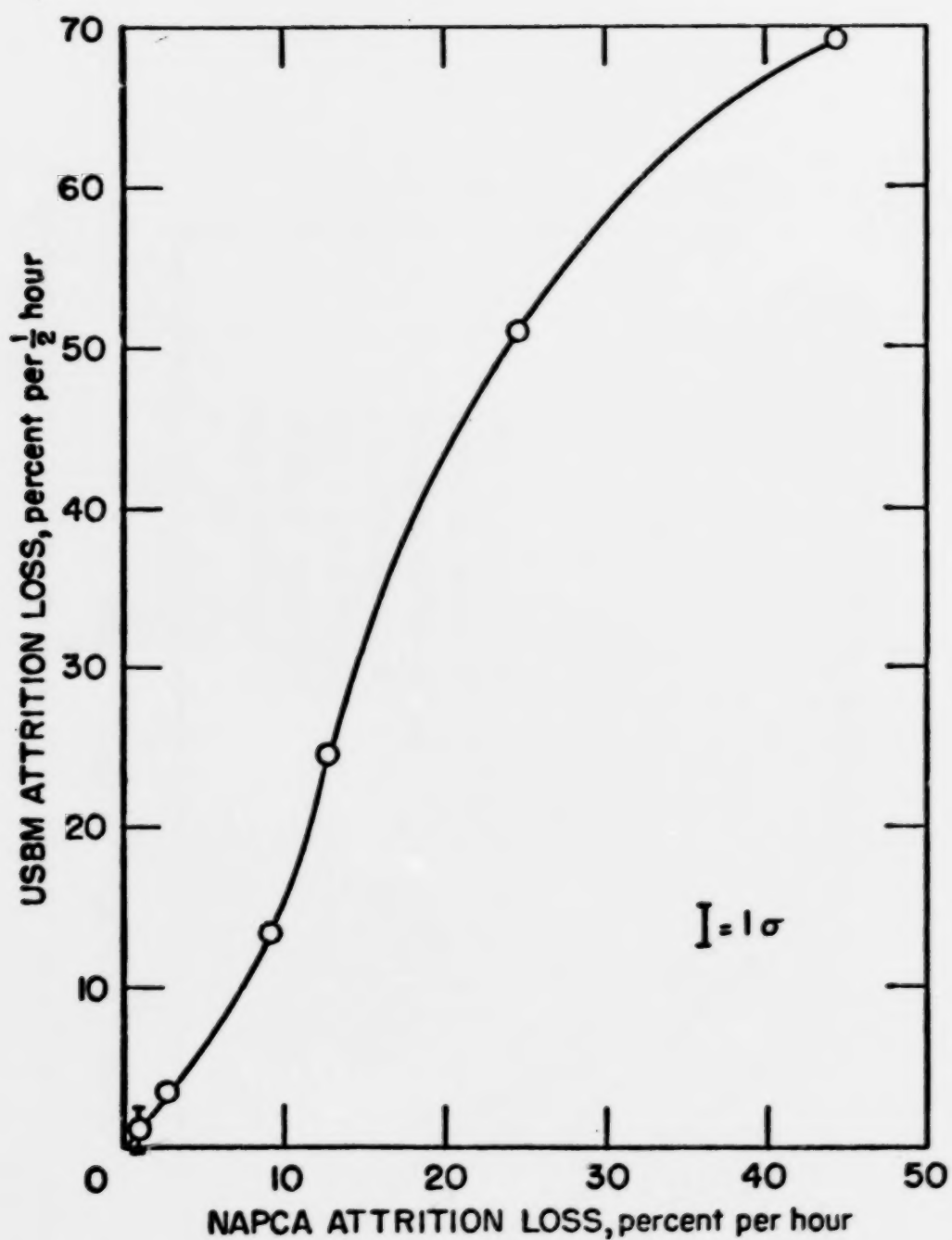


FIGURE 10 -Attrition loss as measured by USBM and NAPCA tests

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is shown in Figure 11. It should be noted, however, that in tests with active sorbents, USBM had used a 10/1 sorber recycle ratio while Figure 11 indicates a recycle ratio of only 2/1. Since about the same pressure drop was obtained in both cases, the sorbent density in the reactor was the same and SO₂ removal should be satisfactory. If a higher recycle ratio is found to be necessary to obtain adequate SO₂ removal, then a greater attrition loss is likely. Despite this possible deficiency, however, the data are quite useful in showing the relationship between laboratory and pilot plant results. Also, the data indicate that the attrition resistance of the UOP catalyst support is in the range that will be required for a commercially acceptable sorbent.

(2) Impregnation on UOP Catalyst Support

The high porosity of the UOP support suggested that an active, attrition resistant sorbent might be prepared by impregnation, and consequently sodium aluminate and copper sulfate both are presently being evaluated as impregnants for the UOP support. USBM has observed that regeneration at standard conditions has been incomplete, resulting in loss of sorption capacity during subsequent cycles but more study involving this sorbent preparation is needed before any definite recommendations can be made.

(3) Binder Strengthened Alkalized Alumina

(a) USBM Fillers and Mortar Types

Addition of binders was also studied as a means of improving attrition resistance of alkalized alumina filter cake. USBM tried fillers and mortar type materials which do not require heat treatment to set. Preparation and test procedure consisted of blending the binder with wet filter cake and then forming approximately 3/32 inch ex-

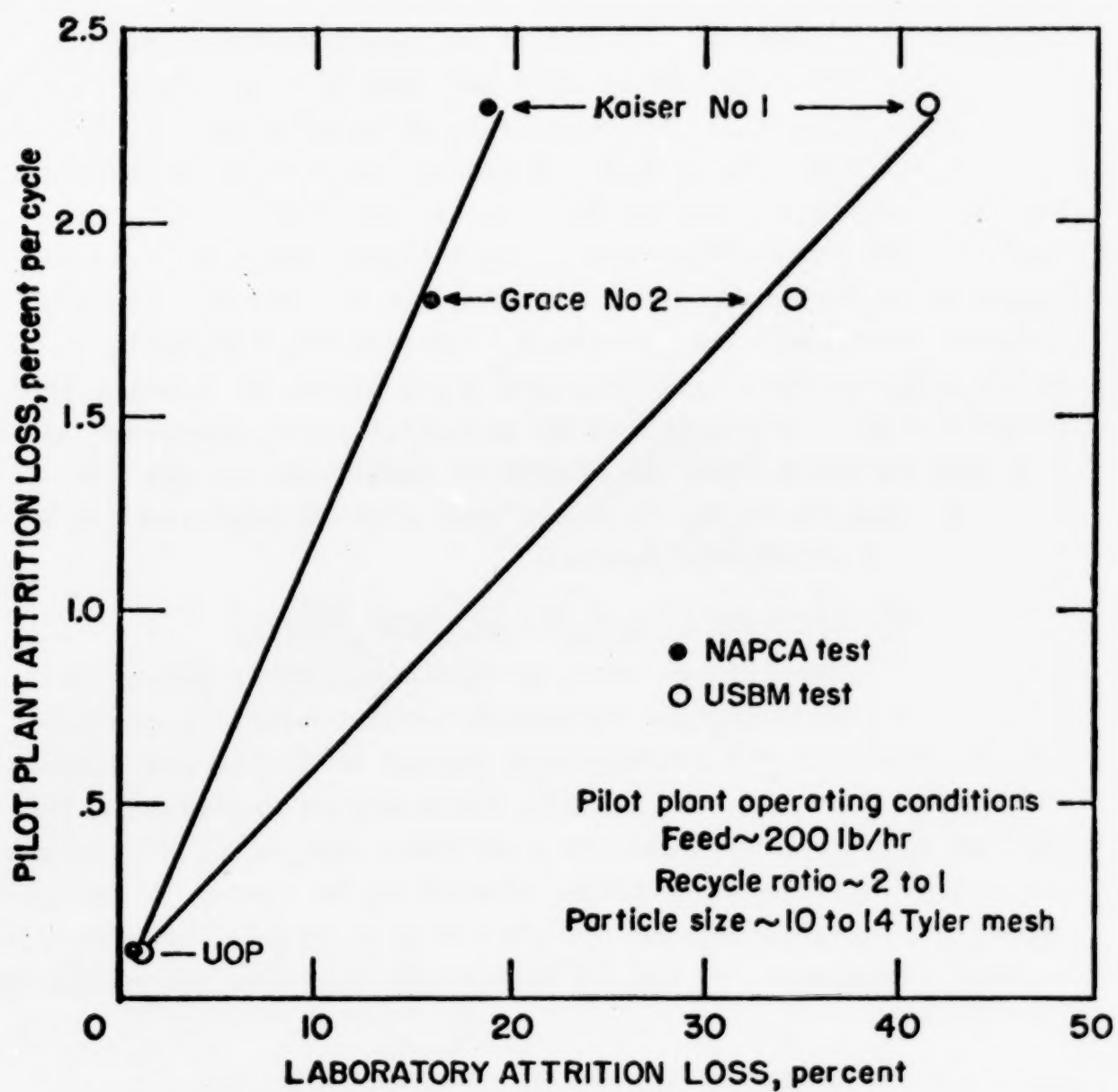


FIGURE 11 - Pilot plant sorbent loss predicted from laboratory tests

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trudates which were dried in air at 220 to 230°F. After normal activation, the sorbents were exposed to flue gas in the pilot plant for 24 hours and then regenerated with hydrogen for 10 hours at 1200°F. Binders added to alkalized alumina filter cake have improved its resistance to degradation, but long term stability and optimum binder concentration are not yet known. Three materials were found which need further study. One contains asbestos fibers, while the other two contain a chemically setting potassium silicate mortar. The best sample (USBM-CMBI) had an attrition loss of 19.4% USBM basis (12% by NAPCA/AVCO test) after 2 sorption-regeneration cycles.

(b) W. R. Grace Studies

Grace investigated sodium aluminate bound with kaolin or meta-kaolin and concluded that the attrition resistance was not satisfactory. Similar results were obtained with cement bound Dawsonite samples for curing conditions of 100% steam up to 700°F. Also, variations in attrition characteristics of different lots of Dawsonite bound by kaolin and sodium silicate were obtained as can be seen in Table 4. Material from the fifty pound sample, CD-131, was subjected to 84 cycles in the portable field test units. Attrition of this material remained constant at 6% (AAJA 2nd degree NAPCA or AVCO test) during this period. Calculations in conjunction with Na_2O and CO_2 analyses show a possible difference in the Dawsonite base material from spray dried lots 1 and 2 and Grace states that X-ray confirms this possibility. However, further data are needed to correlate this observation with forming characteristics and attrition behavior.

(c) NaAlO_2 Pellets Prepared from BSAC Intermediates

A series of attrition tests were run in order to evaluate various BSAC (Basic Sodium Aluminum Carbonate intermediates) materials prepared at the Albany Metallurgy Research

TABLE 4

VARIATION IN ATTRITION RESISTANCE

OF

RL-175 COMPOSITION ALKALIZED ALUMINA

(DAWSONITE BOUND WITH 23% KAOLIN AND 2% Na₂SiO₃)

<u>DAWSONITE BASE</u>	<u>SAMPLE LOT NO.</u>	<u>POUNDS MADE</u>	<u>SINGLE CYCLE EVALUATION</u>	
			<u>WT % S SORBED</u>	<u>ATTRITION</u>
1st Spray Dried Lot	CD-131	50	7-8	6-10%
2nd Spray Dried Lot	CD-132	200	6-8	65-75%
2nd Spray Dried Lot	CD-135	4000	6-8	75-80%

Ref: W. R. Grace and Company, April 1969 Monthly Report, Phase I,
Table 1.

Center. Modified 2nd degree AAJA test parameters were a 60 mesh top screen, 3.45 SCFM air velocity, 30 gram sample weight and a 1 hour test time, these conditions are identical with those used in the NAPCA/AVCO test. The samples represented materials having crushing strengths from approximately 1 to 20 pounds. After each 1 hour test the samples were replenished to 30 grams total weight. Results of these attrition tests are shown in Figure 12. The following discussion is from a USBM-Albany report and is believed to adequately describe the results.

The apparent decrease in attrition loss over the first three runs as displayed by the stronger materials was expected. The pellets being made on a laboratory scale at AMRC are right cylinders with length to diameter ratios of approximately 1. Therefore, the corners wear off rapidly during the initial attrition exposure and the true attrition resistance of the materials cannot be evaluated until the right cylinders are eroded to approximate spheres. This is indicated by the leveling off of the attrition loss curves shown in Figure 12.

However, the weaker sorbent materials (plots #1, #2, and #3) displayed attrition loss behavior completely different than previously discussed. The material represented by Plot #1 was spherodized before the attrition tests were run and the W. R. Grace material (plot #3) was in the form of irregular spheres. Both material displayed increased attrition losses following the initial one hour test. The attrition behavior of the weaker sorbent materials is attributed to a fracture mechanism instead of attrition.

The results of the above tests show that modifying the basic structure of the alkalized alumina pellets

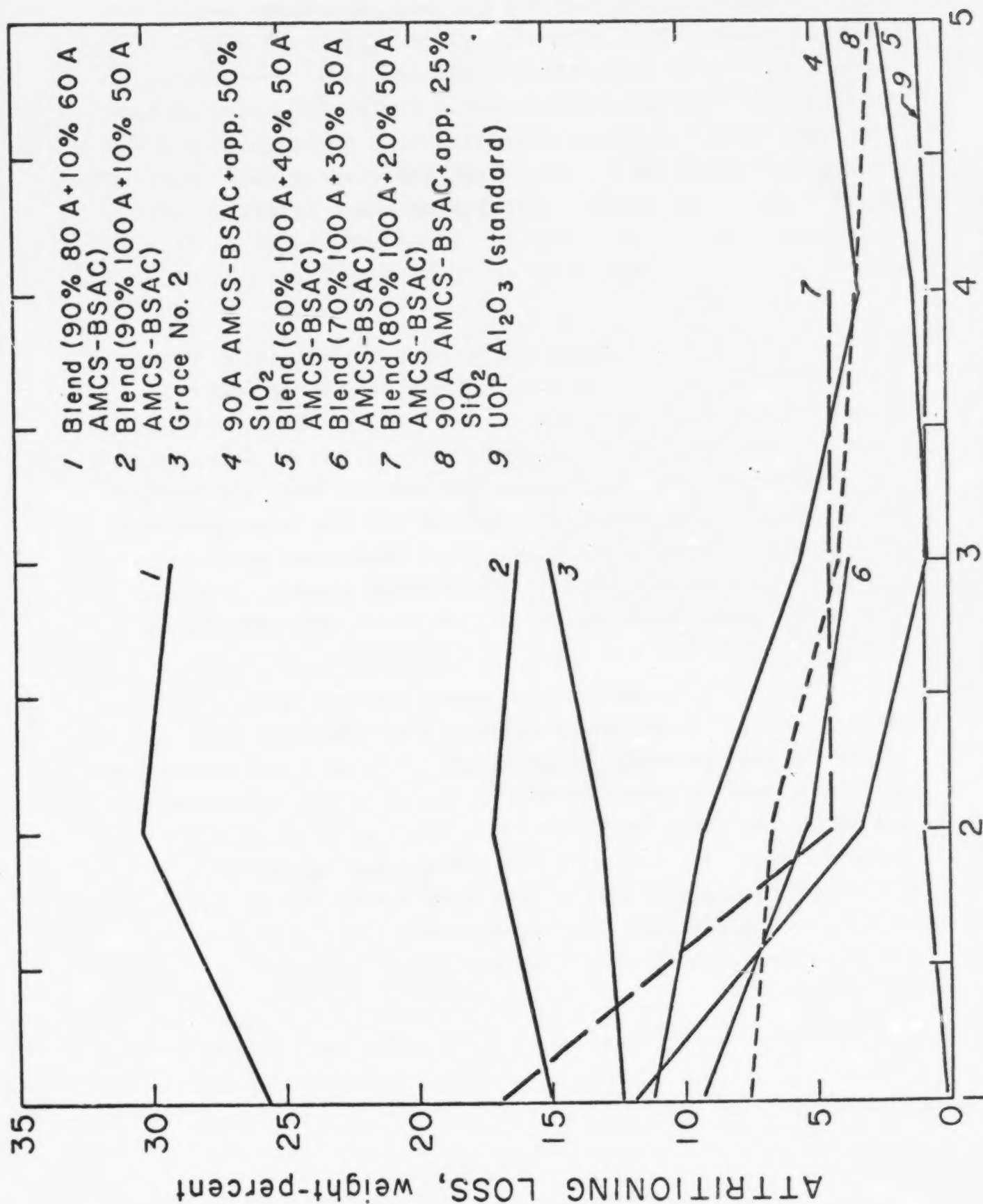


FIGURE 12.-Results of AAJA Attritioning Tests on Activated BSAC Material.

provides improved attrition resistance in some cases, at least on the activated material. Additional tests are required to determine if these improvements are obtained after the sorbent has been subjected to multi-sorption/regeneration cycles. It can be seen from Figure 12 that the UOP alumina sample exhibited very low attrition losses which is consistent with the results of the Bruceton tests.

2. Sorption

a. Sorbent Selection

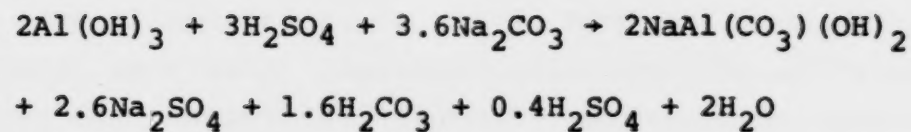
In 1956 the Department of Health, Education, and Welfare initiated a study with the United States Bureau of Mines (USBM) to screen existing processes and examine the possibility of developing new materials or processes for the removal of sulfur dioxide (SO_2) from flue gases. After long and intensive study a new material (alkalized alumina) was selected. In the intervening years, the alkalinized alumina chemisorbent was tested and developed to the extent that a full scale process study was needed to develop process design for a commercial size plant based on this sorbent, with the objective of determining technical and economic feasibility.

b. Sorption Chemistry

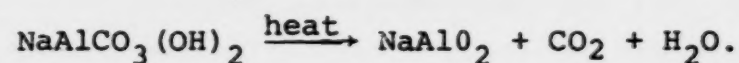
(1) Sorbent Preparation

Although many methods have been developed to produce alkalinized alumina, the basis of all these processes is the production of Dawsonite, $\text{NaAlCO}_3(\text{OH})_2$, as the intermediate product. The production of Dawsonite by the original Bienstock patent¹ is typical:

¹ Bienstock, D. and Field, J. H., Process for the Removal of Sulfur from Gases, U. S. Patent 2,992,884, July 18, 1961.



The solid Dawsonite formed by the reaction is filtered, washed to remove sulfur (SO_4), and dried. The dried solids are then activated by heating in a 600°C reducing atmosphere to remove any sulfur remaining in the Dawsonite intermediate, and to drive off carbon dioxide and water thus leaving the basic sorbent, sodium aluminate, NaAlO_2 :

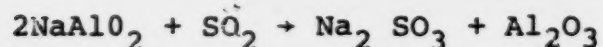


The solid product of the reaction, sodium aluminate, comprises what is commonly known as alkalized alumina.

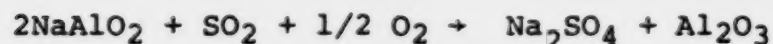
(2) Sorption Reaction

There are two chemical reactions which have generally been accepted as representing the sorption of SO_2 by alkalized alumina. These reactions are as follows:

1. Sodium aluminate reacts with the sulfur dioxide in simulated flue gas (does not contain NO_x) to form sodium sulfite and aluminum oxide.



2. Sodium aluminate reacts with sulfur dioxide and oxygen in the flue gas to form sodium sulfate and aluminum oxide.



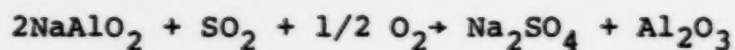
As well as being influenced by NO_x , these reactions are highly temperature dependent. At 120°C in the

absence of NO_x a combination of the two reactions occurs whereas at 330°C , the design temperature used in the sorption process, or in the presence of NO_x , only the second reaction occurs. These conclusions have been verified by the analysis of the reaction products leaving the various laboratory and pilot plant sorbers.

The data in Table 5 (which were obtained using a simulated flue gas) and the following discussion are taken from USBM Report #RC-1331:

The data in Table 5 show that as temperature is increased from 130° to 215°C the sorbed SO_2 tends to convert from sodium sulfite to sodium sulfate and that at 300°C it is all converted to sodium sulfate. However, whether the oxidation of the sorbed SO_2 from sulfite to sulfate takes place before sorption or after sorption has not been determined as yet. The pellet loads obtained in 0.045 percent SO_2 flue gas show that insufficient SO_2 has been sorbed in two hours to convert the primary starting material NaAlO_2 to either Na_2SO_3 or Na_2SO_4 (Form III). As the SO_2 gas concentration is increased the amount of SO_2 sorbed per unit time increases to nearly the theoretical load, converting all the NaAlO_2 to either sulfite or sulfate.

An additional point of interest as to the exact sorption mechanism is that as the NaAlO_2 is converted to either Na_2SO_3 or Na_2SO_4 , the alumina formed during the reaction, as indicated by the equation, is not shown by x-ray diffraction. When the loaded pellets are heated to $1,050^\circ\text{C}$ the alumina crystallizes sufficiently and



has been identified as iota-alumina. Whether or not the amorphous alumina is chemically present in the Na_2SO_4 has

TABLE 5 - X-ray Diffraction Results on Loaded Grace Alkalized-Alumina

SO ₂ gas conc. percent	Temp. ° C	Pellet Load, 1/ gS/gP ^{1/}	X-ray Diffraction		
			Primary	Secondary	Minor
0.049	130	0.039	Na ₂ SO ₃ Na ₂ Al ₂ O ₄ Na ₂ Al ₂ O ₄ Na ₂ Al ₂ O ₄ --	--	Na ₂ SO ₄ Na ₂ SO ₄ Na ₂ SO ₄ Na ₂ SO ₄ --
.045	215	.034			
.045	300	.032			Na ₂ SO ₄
.045	400	.029			--
0.34	130	0.130	Na ₂ SO ₃		Na ₂ SO ₄
.34	215	.125	Na ₂ SO ₃		
.34	300	.097	Na ₂ SO ₄		
.34	400	.069	Na ₂ SO ₄	Na ₂ SO ₄ Na ₂ Al ₂ O ₄	
2.01	130	0.138	Na ₂ SO ₃		Na ₂ SO ₄
2.04	215	.140	Na ₂ SO ₃		
2.07	300	.142	Na ₂ SO ₄		
1.98	400	.136	Na ₂ SO ₄ --	--	--
10	130	0.119	Na ₂ SO ₃		
10	215	.130	Na ₂ SO ₄		Na ₂ Al ₂ O ₄
10	300	.142	Na ₂ SO ₄		Na ₂ Al ₂ O ₄ Na ₂ Al ₂ O ₄
10	400	.142	Na ₂ SO ₄		Na ₂ Al ₂ O ₄

1/ Gas-pellet contact 2 hours

Taken from USBM RI 7275, Table 7.

not been determined at this time; however, additional work is being conducted to identify the exact reactions that take place and to determine the end products formed.

(3) Thermochemistry

Using the heat of formation data reported in the J.A.N.A.F. Thermochemical Tables (see Table 6), the heat of reaction, ΔH_r , for the sorption of SO_2 at 330°C (626°F) is $-207,350$ Btu/lb mol SO_2 . Using this value for ΔH_r and neglecting the heat picked up by the sorbent, the adiabatic temperature rise of the gas in the sorbers is calculated to be approximately 55°F . This temperature rise is based on the gaseous effluent of a 1000 megawatt coal fired power station using a 3% sulfur coal and the reaction proceeding to the sodium sulfate form.

In the commercial designs this heat of reaction will be used to compensate for heat losses in the system. Therefore, the value of ΔH_r should be verified by experimental data to substantiate the assumption of an essentially isothermal system which has been made in these commercial designs. At the time of this writing, however, no data have been received to verify the theoretical value calculated from J.A.N.A.F. data.

(4) Sorption Kinetics

In the early stages of experimentation the USBM at Bruceton, Pennsylvania investigated the sorption kinetics of alkalized alumina in two different types of gas-solids contractors, namely a fixed bed, and a dilute phase falling bed. A significant observation was the difference between the rate constants as calculated for the fixed and falling bed reactors. The constant associated with the falling-bed was greater than that for the packed column.

TABLE 6
HEATS OF FORMATION DATA¹

<u>MATERIAL</u>	<u>ΔH_f @ 600°K*</u>	<u>ΔH_f @ 700°K*</u>	<u>ΔH_f @ 626°F**</u>
NaAlO ₂	-271.568	-271.436	-271.564
Al ₂ O ₃	-400.304	-400.098	-400.298
Na ₂ SO ₄	-330.874	-330.386	-330.859
SO ₂	-72.824	-73.206	- 72.835
O ₂	--	--	--

1 Reported in Kcal/mol.

* From JANAF Thermochemical Tables.

** By linear interpolation.

The difference is not entirely unexpected since there is no reason to assume that the rate controlling mechanism is the same in both cases. The effective solid density in the falling bed is much less than in the fixed bed, so that possibly gas diffusion is controlling in the former system. However, the higher rate constant in the falling bed, together with the fact that the fixed bed performed at a greater efficiency than predicted in the initial stages of operation, is significant. One plausible explanation is that in the early stages of gas-solids contact the reaction of SO_2 on the surface of the particle is controlling. Later when the surface is covered with reaction products, diffusion into the particle (which occurs at a much slower rate than the surface reaction) becomes controlling. It is this slower diffusion step which is important in the long run behavior of the fixed bed reactor.

In the falling bed experiments the solids residence time is very small (on the order of 15 seconds to a few minutes) as compared to exposure time in the fixed bed system of 200 to 300 minutes, and fresh sorbent is constantly fed to the falling-bed sorber while the sorbent in the fixed bed sorber is constantly being loaded with sulfur. Thus it is conjectured that in the falling bed contactor only the rapid surface reaction is occurring, which in turn helps to explain the larger rate constant calculated for this system.

In an attempt to test this hypothesis, some theoretical curves have been computed for the fixed bed reactor assuming (1) only the rapid surface reaction is taking place, (2) pore diffusion is controlling. These curves are shown in Figures 13, 14, and 15. The curves indicate that the hypothesis is correct. The initial sorption reaction is accurately predicted by the assumption of a gas film

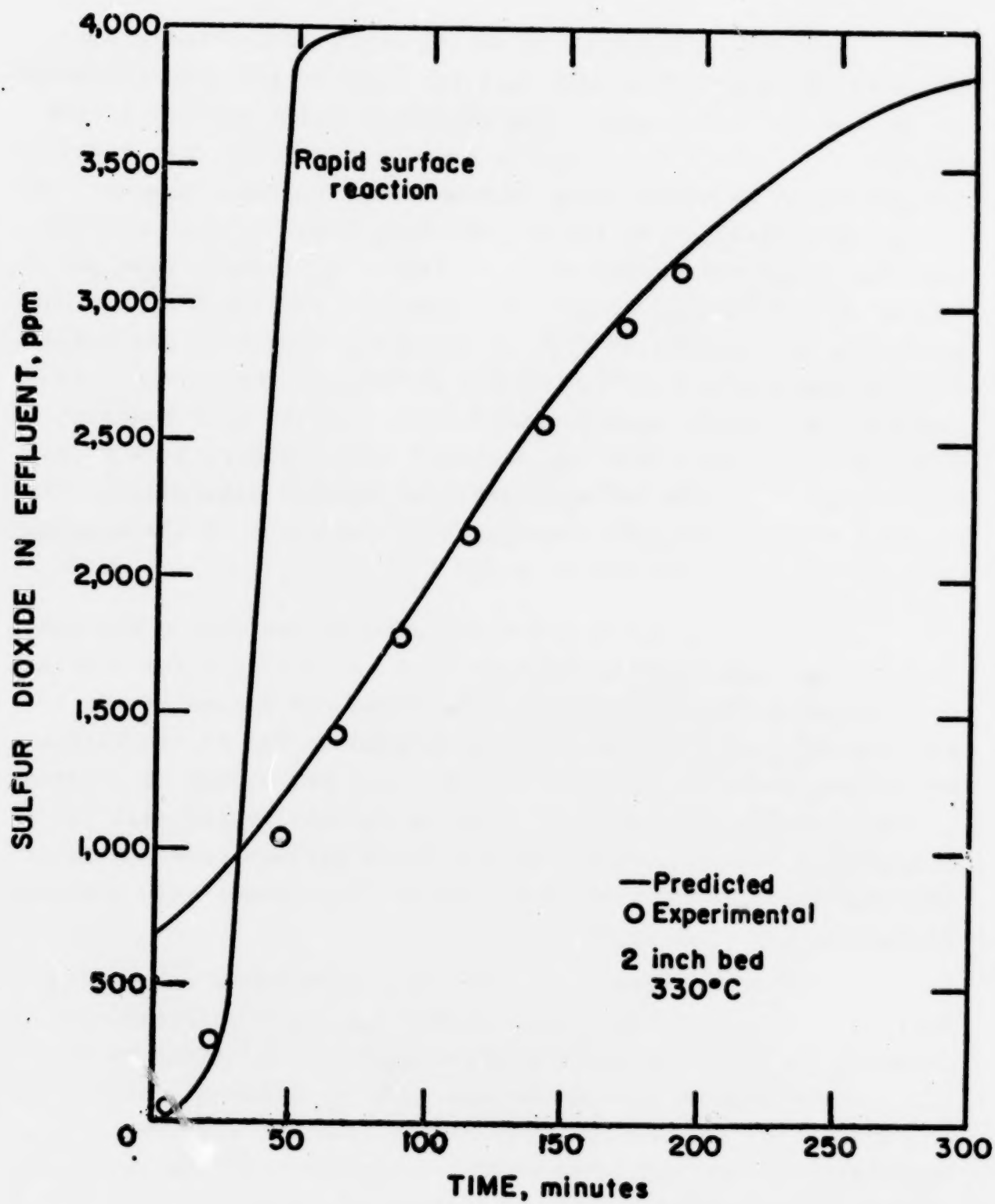


FIGURE 13 - Experimental removal of sulfur dioxide and predicted removal when surface reaction is controlling and when diffusion is controlling in a 2-inch packed bed of alkalinized alumina.

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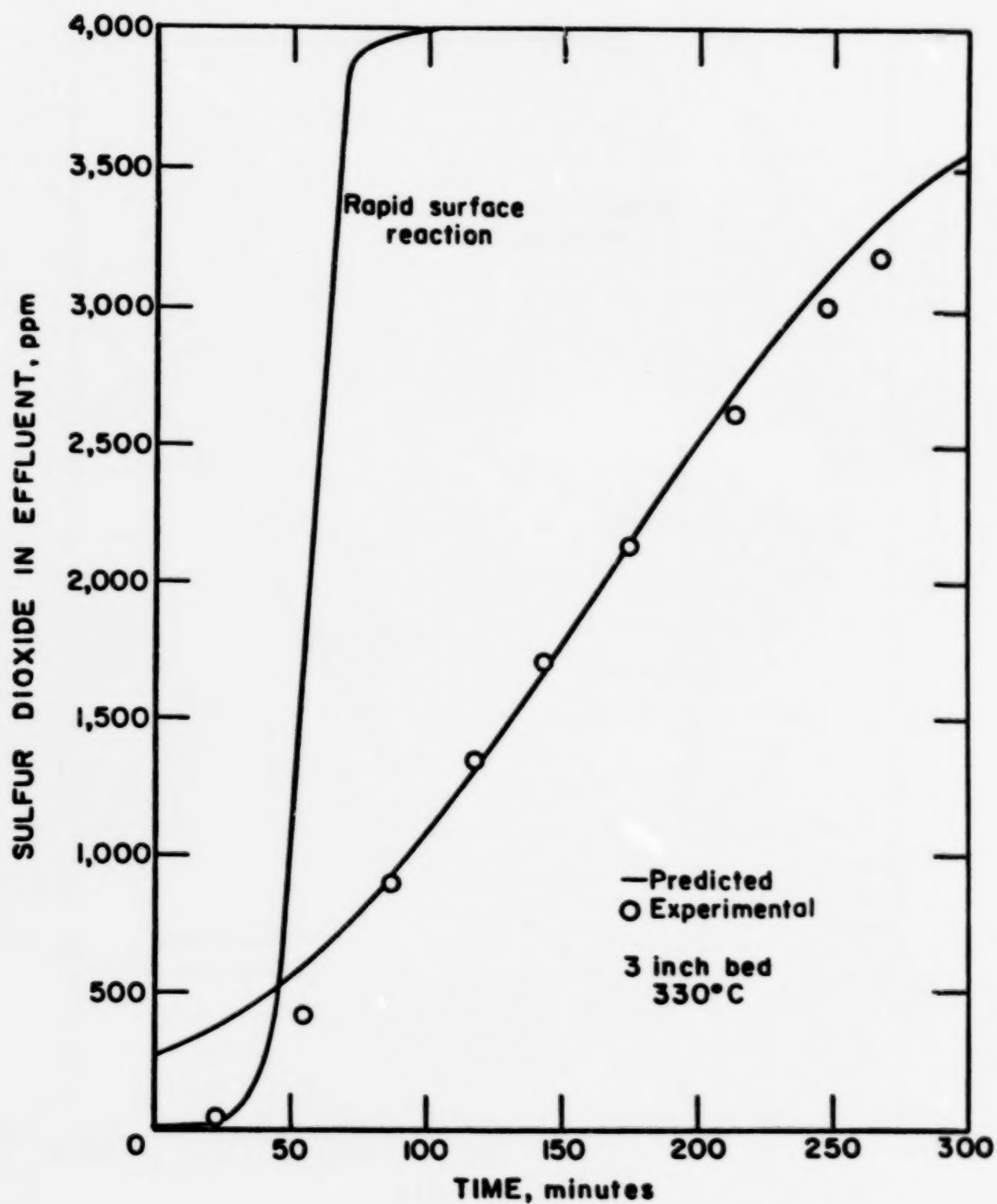


FIGURE 14-Experimental removal of sulfur dioxide and predicted removal when surface reaction is controlling and when diffusion is controlling in a 3-inch packed bed of alkylized alumina.

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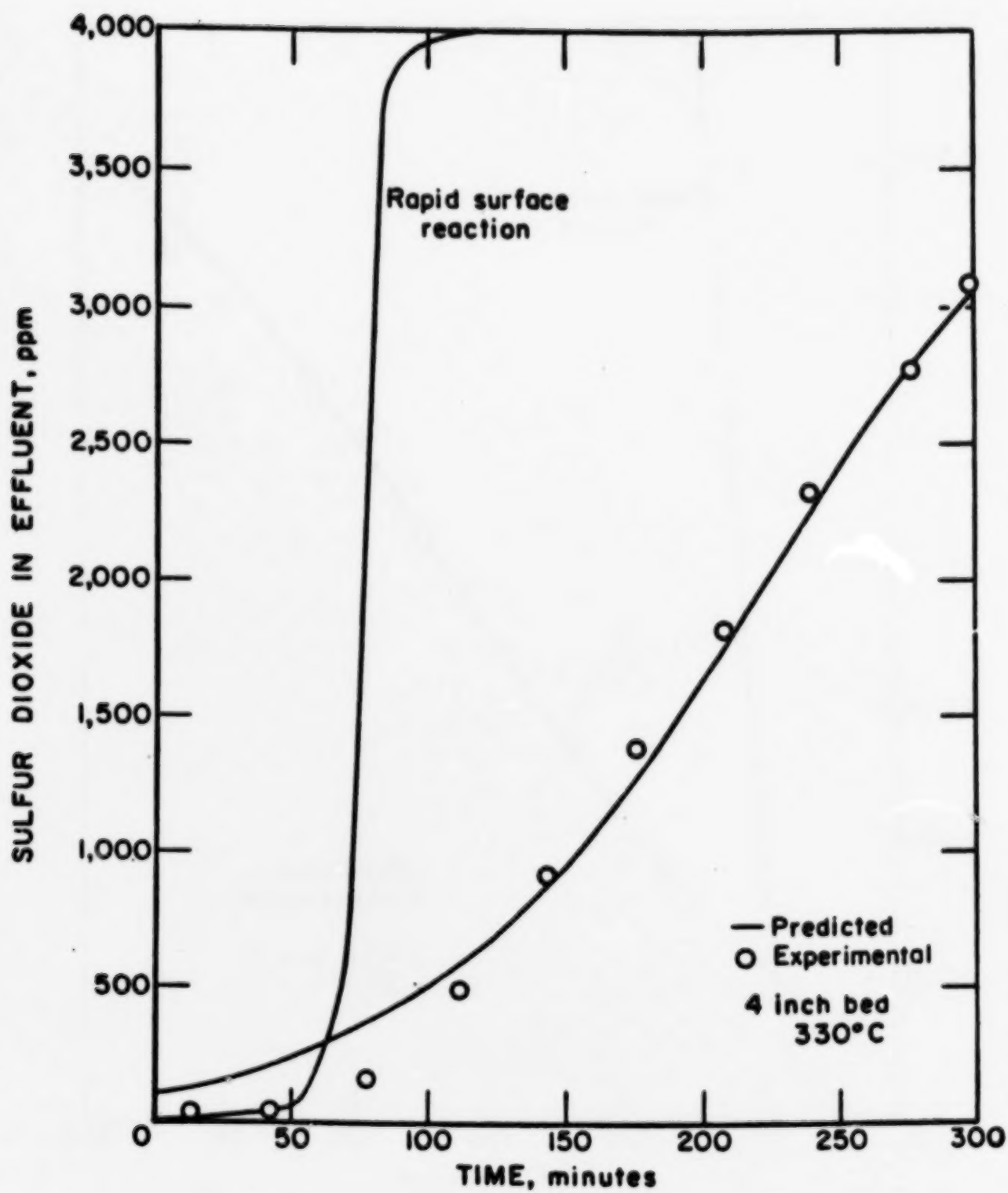


FIGURE 15 - Experimental removal of sulfur dioxide and predicted removal when surface reaction is controlling and when diffusion is controlling in a 4-inch packed bed of alkylized alumina.

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L-9080

controlling mechanism while the data after the initial sorption are supported by a pore diffusion controlling model. A further proof of the initial surface reaction can be seen in that the duration of the reaction is a function of the bed height, i.e., the higher the bed and thus the larger the surface area, the longer the applicability of the gas film control. These figures also show a definite transition region between the two mechanisms with the region defined by the bed height investigated.

Although the rapid surface reaction would be preferable in reactor design, the constraints of attrition, regeneration and the relatively small surface (excluding pore surface) of the sorbent prohibit the use of this mechanism as the basis for designing the actual process unit. The sorption reaction is limited, therefore, to the relatively slower pore diffusion mechanism. However, this does not demean the quality or capacity of the sorbent, for it remains superior to the other potentially commercial sorbents tested.

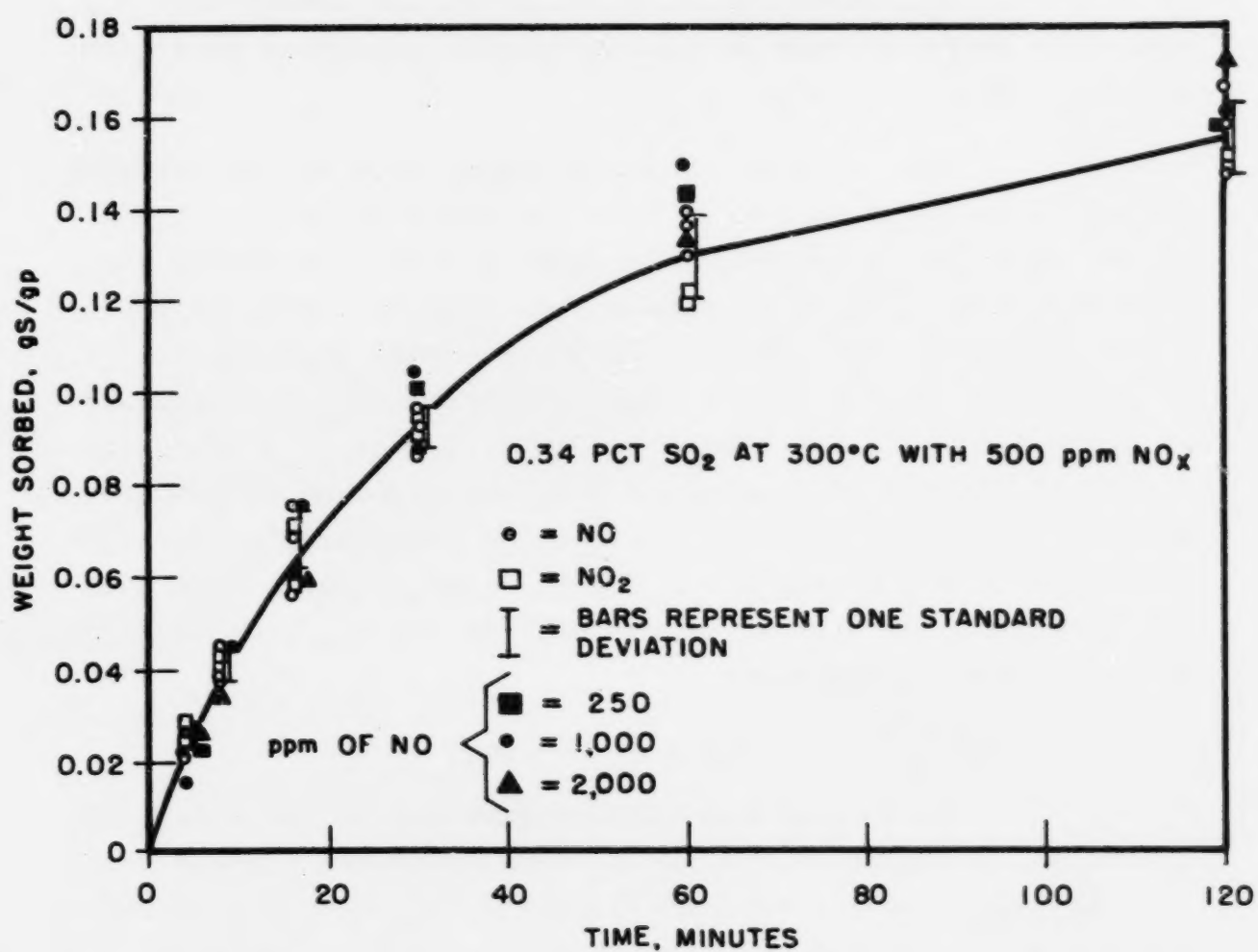
In the preliminary sorption studies most of the investigators produced a synthetic flue gas by mixing the appropriate major flue gas constituents of N_2 , O_2 , CO_2 , SO_2 , and H_2O . However, the AVCO Corporation found that oxides of nitrogen (NO_x), which are present in small quantities in actual flue gases and had been omitted by the earlier investigators, improved the sorption rates of SO_2 on alkalized alumina. Consequently, an evaluation of the sorption rates of SO_2 in the presence of either nitric oxide, NO , or nitrogen dioxide, NO_2 , was undertaken by the USBM at Albany, Oregon, to determine the extent of this improvement.

Their results show that either nitric oxide (NO) or nitrogen dioxide (NO_2) increased the sorption rate such that a 0.10 gS/gP load was obtained in about 33 minutes as compared to about 120 minutes for the standard runs made

without nitrogen oxides (NO_x) present. The actual sorption rate obtained with NO_x under standard test conditions (300°C , 0.34% SO_2 , 0.10 gS/gP) was 5.05×10^{-5} gS/gP/sec, whereas the rate without NO_x was 1.44×10^{-5} gS/gP/sec. The effect of NO_x concentration on sorption rate was also determined by running tests in which the level of NO_x was varied from 250 to 2000 ppm. The results of these NO_x tests are shown in Figure 16, which is taken from USBM RI 7275, pp 23-24, while the standard run results are shown in Figure 19, from page 17 of RI 7275. The Figure 16 curve has been drawn through the 500 ppm points and the data points for the other NO_x levels are shown. The results in Figure 16 show that while there is some variation of sulfur load for each contact time, all of the points fall along the 500 ppm line. Based on these results it is concluded that, within the limits of the test conditions, the presence of NO_x increases the SO_2 sorption rate by 2 to 3.5-fold but the concentration of NO_x appears to have a negligible effect. Additional tests were run at different SO_2 concentrations (0.045 to 10%) and similar results were obtained; i.e., sorption rate increases of 2 to 3.5-fold over those without NO_x .

The effect of temperature on sorption rate was determined by running a series of tests at 215° and 130°C with 500 ppm NO_x in the flue gas. The results of these tests are shown later in this report as Table 9 which is from a USBM-Albany yearly report dated June 30, 1969. From Table 9 it is apparent that when the temperature is decreased not only does the sorption rate decrease but the effect of NO_x on sorption rate decreases also. For example, at 0.34% SO_2 and a pellet load of 0.05 grams sulfur/gram pellet, the average sorption rates for 300; 215; and 130°C are 7.94, 5.95, and 4.38×10^{-5} gS/gP/sec respectively, or a 1.8-fold decrease. The corresponding ratio of sorption rates with NO_x to those without NO_x are

FIGURE 16
EFFECT OF NO_x ON SO₂ SORPTION AT 300°C
IN
0.34 PCT SO₂ FLUE GAS

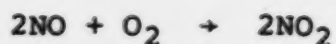


REFERENCE:
USBM RI 7275, Figures 14 and 15.

3.0, 144, and 0.78 or a 3.85-fold decrease. It is interesting to note that the effect of NO_x on sorption rate reverses at the lower temperature; i.e., at 130°C , adding NO_x causes the sorption rate to decrease.

USBM-Albany also did some work in an attempt to determine the mechanism by which the presence of NO_x increases the sorption rate. The results are discussed in RI 7275, part of which is reproduced below, and support the theory that NO_x increases sorption rate by increasing the oxidation of SO_2 to SO_3 or Na_2SO_3 to Na_2SO_4 .

The increase in SO_2 sorption rate in the presence of NO_x is believed to result from increased oxidation of SO_2 to SO_3 or Na_2SO_3 to Na_2SO_4 . To substantiate this theory X-ray diffraction analyses were obtained on samples loaded at 130° , 215° , and 300°C . The results in Table 7 show that the SO_2 sorbed formed Na_2SO_4 at all three temperatures. A comparison of these data with the results in Table 5, wherein at 130°C the sorbed SO_2 formed Na_2SO_3 , shows that the nitrogen oxides are actually improving the sorption rate by increasing either the oxidation of SO_2 to SO_3 or Na_2SO_3 to Na_2SO_4 . The reason that the sorption rate with NO is the same as the NO_2 rate is shown by the following equation:



To further resolve the question of the effect of oxidation on sorption rate, tests were conducted wherein the 0.34 pct SO_2 flue gas was passed over a V_2O_5 catalyst to convert the SO_2 to SO_3 before sorption onto the alkalized alumina. Because of the low oxygen content in the flue gas only 60 pct of the SO_2 was converted to SO_3 at 500°C . Results of the SO_3 test are given in Table 7 and show that with the SO_3 in the flue

TABLE 7 - X-ray diffraction results for Grace alkalized alumina loaded
in the presence of nitrogen oxides

Test con- ditions	SO ₂ con- centration, pct	Temper- ature, ° C	Pellet load, gS/gp ¹	X-ray diffraction analyses			
				Primary	Sec- ondary	Minor	Trace
250 ppm NO.	0.34	300	0.157	Na ₂ SO ₃	-	-	-
500 ppm NO.	.34	300	.158	Na ₂ SO ₄	-	-	-
1,000 ppm NO.	.34	300	.158	Na ₂ SO ₃	-	-	-
2,000 ppm NO.	.34	300	.170	Na ₂ SO ₄	-	-	-
500 ppm NO.	.34	300	.152	Na ₂ SO ₃	-	-	-
500 ppm NO.	.34	215	.150	Na ₂ SO ₄	-	-	-
500 ppm NO.	.34	130	.113	Na ₂ SO ₄	-	-	Na ₂ Al ₂ O ₄
500 ppm NO ₂	.34	300	.150	Na ₂ SO ₄	-	Na ₂ Al ₂ O ₄	NaNO ₃
500 ppm NO ₂	.34	500	.080	Na ₂ SO ₄ , Na ₂ Al ₂ O ₄	-	Na ₃ Al(SO ₄) ₃	-
60 pct SO ₃ ...	.34	500	.136	Na ₂ SO ₄	-	Na ₃ Al(SO ₄) ₃	-
Standard run.	.34	500	.092	-	-	-	-

¹Gas-pellet contact time 2 hr.

Taken from USBM RI-7275, Table 9.

gas, Na_2SO_4 is formed and a pellet load of 0.136 gS/gP was obtained in 2 hr. The sorption rate for a pellet load of 0.100 gS/gP was 3.9×10^{-5} gS/gP/sec which is less than the rate of 5.05×10^{-5} gS/gP obtained for the standard runs using NO_x . It should be noted, however, that the SO_3 run was at 500°C instead of 300°C and as shown in Table 7, the runs with and without NO_x at 500°C have lower pellet loadings (hence lower sorption rates) than at 300°C. For example, the 500 ppm NO_2 run shows a pellet loading of 0.150 gS/gP at 300°C and only 0.080 gS/gP at 500°C, while the standard run without NO_2 achieved a loading of 0.092 gS/gP at 500°C. Based on the data in Table 7 it appears that SO_3 is sorbed faster than SO_2 even when NO_x is present but no firm conclusions can be drawn because insufficient data are presented to fully define the temperature effect.

Further discussion of the NO_x effect will be contained in section 2-b-(5) of this report. Similarly, the actual sorption data and eventual modeling of the kinetic data will be presented in separate sections of this report.

(5) Extraneous Chemical Effects

Aside from the basic sorption reactions mentioned earlier, various other side reactions influence the sorption of SO_2 on alkalized alumina. The chemicals causing these side reactions were found to be:

(a) Chlorides

The reaction of chlorine compounds found in flue gases has given some cause for concern throughout the development of the sorbent. Experimental work by the Central Electricity Generating board of Great Britian, C.E.G.B., showed that a synthetic flue gas containing hydrogen chloride

and SO_2 led to a rapid reaction of chlorine on to the sodium aluminate. This chlorine was not displaced during the regeneration process so that the build-up was cumulative. Once the chlorine concentration reached about 10% it severely reduced the sorptive capacity of the sodium aluminate, while at about 12% chlorine, the sorbent became completely inactive toward SO_2 . Work at the USBM-Bruceton also confirmed this cumulative build-up under laboratory conditions.

However, results from the C.E.G.B. continuous recycling rig at Blyth which operates on actual flue gases, showed that the behavior of chlorine was completely different from that in the laboratory. There was a small uptake during the first few cycles, after which time no further chlorine was retained on the reactant. The reasons for this are still not certain, but it is possible that the oxides of nitrogen may be important in oxidizing SO_2 to SO_3 . It may be that sulfur trioxide can displace hydrogen chloride, while sulfur dioxide is incapable of making this replacement. Thus the catalytic oxidation of sulfur dioxide on the surface of the reactant could be the reason why chlorine is not troublesome when power station flue gases are used. Regardless of the actual mechanism, the important point with respect to process design is that chlorine does not deactivate the sorbent.

(b) Water

The effect of water or steam concentration on the sorption of SO_2 by alkalized alumina is shown in Table 8. These data, which were obtained by the W. R. Grace Company, indicate that a minimum 2.5% steam concentration, comparable to the levels obtained in a power plant effluent, is necessary during sorption to maximize SO_2 pickup. A similar effect on total capacity was also shown in work by the USBM. The precise

TABLE 8

EFFECT OF WATER VAPOR CONCENTRATION ON SO₂ ABSORPTION RATE¹

<u>H₂O Vapor Concentration</u>	<u>VHSV</u>	<u>Breakthrough Time</u>	<u>Wt. % Gain @ Break</u>	<u>Wt. % Gain @ 150 min</u>
0%	4000	41 min.	3.95	7.47
1%	4000	50 min.	5.02	10.16
2.5%	4000	86 min.	8.27	12.86
5.0%	4000	90 min.	8.69	13.34

¹ W. R. Grace Co., Interim Report 10-31-67, pg. 22.

role of water vapor in the sorption mechanism is unknown; however, the data clearly show that its presence is required. A detailed analysis of this effect by the AVCO Corporation is contained in Appendix B, which, although this analysis is not conclusive, provides further insight into the phenomenon.

(c) Oxygen

Despite the stoichiometric requirement for oxygen in sulfate formation from sodium aluminate (see section b-(2)), a direct demonstration of this requirement was lacking. Consequently, W. R. Grace ran tests in which the oxygen concentration was varied and the results, which are plotted in Figure 17, show that oxygen concentrations less than about 1% significantly decrease sorption rates. Comparison of the 1% oxygen level with the standard synthetic flue gas composition containing 4.5% oxygen shows little change in sorption efficiency at the higher oxygen level. The importance of oxygen in the nitrogen chemistry will be discussed further in the next section of this report.

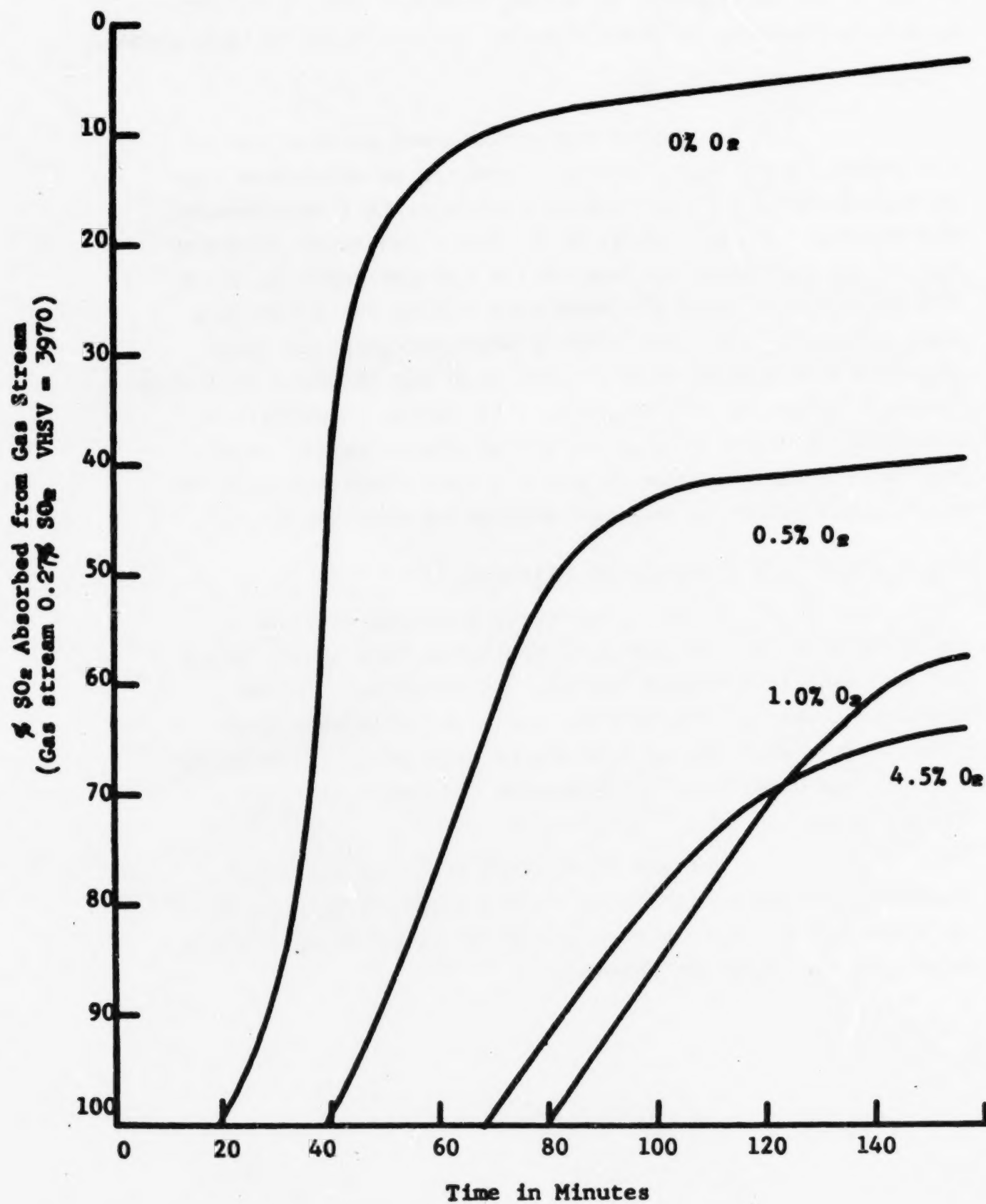
(d) Oxides of Nitrogen

During the early sorption studies laboratory tests were run with synthetic flue gases, which did not contain nitrogen oxides. In later pilot plant testing it was discovered that reaction rates were many times higher when actual flue gases were used. Therefore, a study was undertaken to determine the cause of these higher rates.

It was discovered that the nitrogen chemistry played a vital role in the sorption of SO_2 by alkalized alumina in that oxides of nitrogen apparently catalyzed the sorption reaction.

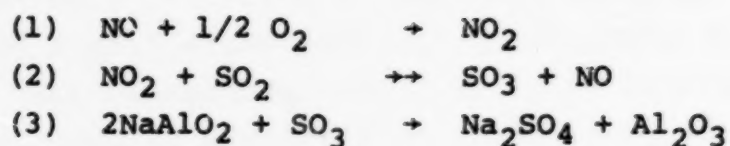
FIGURE 17

EFFECT OF O_2 CONCENTRATION ON ABSORPTION
RATE OF STANDARD ALKALIZED ALUMINA AT $660^\circ F$



In the combustion reaction a small fraction of the nitrogen in the combustion air and/or in the coal is oxidized to nitric oxide, NO, or nitrogen dioxide, NO₂, and these nitrogen oxides are present in power plant flue gases from a range of about 150 to 1500 parts per million. It was found that NO₂ reacted with SO₂ to form sulfur trioxide, SO₃, which is much more reactive with alkalized alumina than is SO₂. Further, thermodynamic calculations show that NO can be oxidized to NO₂ in the proposed sorption temperature range, thus catalyzing the sorption reaction.

The chain of reactions involved in the sorption of SO₂ on alkalized alumina may therefore be written as follows:



Reaction (1) oxidizes the nitric oxide to nitrogen dioxide. Reaction (2) oxidizes the sulfur dioxide to trioxide and returns the nitrogen dioxide to nitric oxide for further oxidation. The sulfur trioxide formed by reaction (2) then reacts with sodium aluminate by reaction (3) to form sodium sulfate and aluminum oxide. The above reactions represent the probable intermediate steps in the basic sorption reaction mentioned previously (Section B-2). The effect of the oxides of nitrogen is a catalytic one in that they are involved in the reaction but returned to their former state. For a detailed discussion of the thermodynamic equilibria involved in the nitrogen oxide chemistry see Appendix C of this report.

c. Sorption Data

(1) Sources

For the development of the various phases of the alkalized alumina process, the Public Health Service (PHS) of the Department of Health, Education, and Welfare awarded contracts to several different organizations. These organizations are the USBM at Albany, Oregon and Bruceton, Pennsylvania; W. R. Grace and Company; and the AVCO Corporation. The PHS has also worked hand in hand with the Central Electricity Generating Board (C.E.G.B.) of Great Britain who at one time considered piloting an alkalized alumina sorption system, sized to treat the flue gases from a 50 megawatt power station, at Blyth, Northumberland. The following discussions will describe the areas in which these investigators have been working as well as present some of the pertinent data and conclusions reached by them in the area of sorption.

(2) USBM - Albany

The USBM at Albany, Oregon has been prolific in both the amount and variety of its data and analyses in the area of alkalized alumina sorption. Initially, their responsibility involved the determination of both the sorption rates of SO_2 on alkalized alumina and the variables which affect these rates. This initial work was done on the apparatus shown in Figure 18.

A synthetic flue gas consisting of N_2 , O_2 , H_2O , and SO_2 is passed through a thin bed (i.e., one layer) of alkalized alumina pellets. The pellet charge, approximately 0.5 grams, is placed in a stainless steel container and supported on an 80 mesh stainless steel screen which insures

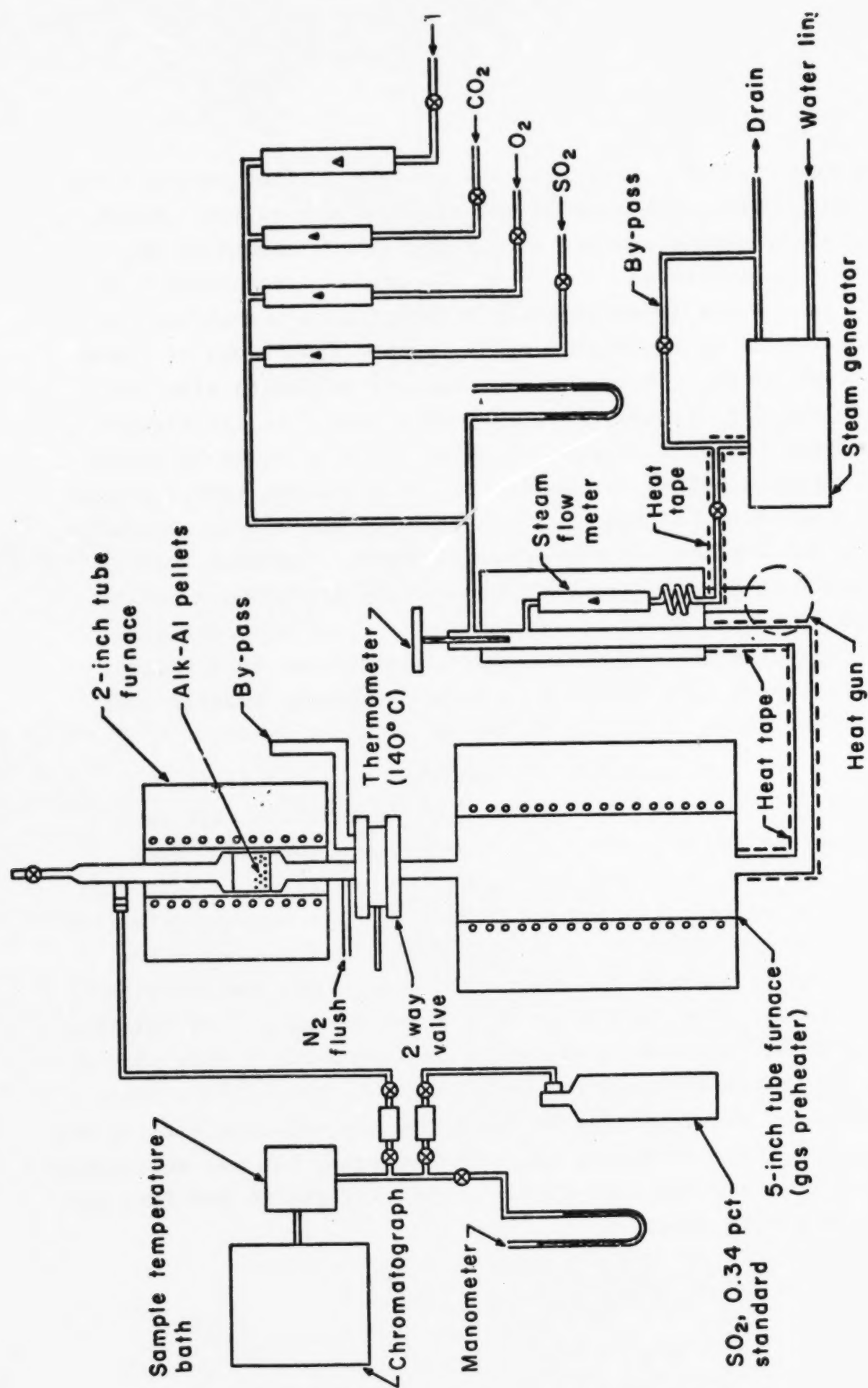


FIGURE 18 - SO₂ Sorption System.

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uniform contact between gas and pellets. After sorption the loaded pellets are removed and analyzed for sulfur. Since the small sample removes only a negligible amount of SO_2 from the gas stream, the inlet and outlet concentration of SO_2 in the gas is essentially constant thus permitting the measurement of the amount of SO_2 sorbed from a gas of fixed concentration. Individual samples are contacted with the flue gas for periods of time ranging from 1 to 120 minutes, analyzed for sulfur, and the pellet load in grams of sulfur per gram of pellet determined for each contact time. A plot of these data is then used to determine the average sorption rate for a given set of test conditions. Standard test conditions are: a reaction temperature of 300°C , a pellet load of 0.5 grams of alkalized alumina, and a superficial gas velocity of 0.18 ft/sec which corresponds to a 31,100 hourly space velocity. Using this technique, results such as those shown in Figure 19 may be obtained.

By changing the reaction temperature in the apparatus the effect of temperature on reaction rate was determined and the results are shown in Figure 20. They show that as the sorption temperature decreases the sorption rate and sorbent loading increases. It has been hypothesized that for the 25°C test runs the temperature was below that required to provide the activation energy for the reaction to proceed. The results of this inverse temperature relationship is not surprising since the data in Table 1 show that at the lower temperatures the sorption is to the sulfite form; therefore, the diffusion of oxygen to the reaction site is not required thus increasing the sorption rate. It was subsequently found that the addition of oxides of nitrogen to the flue gas reverses this effect.

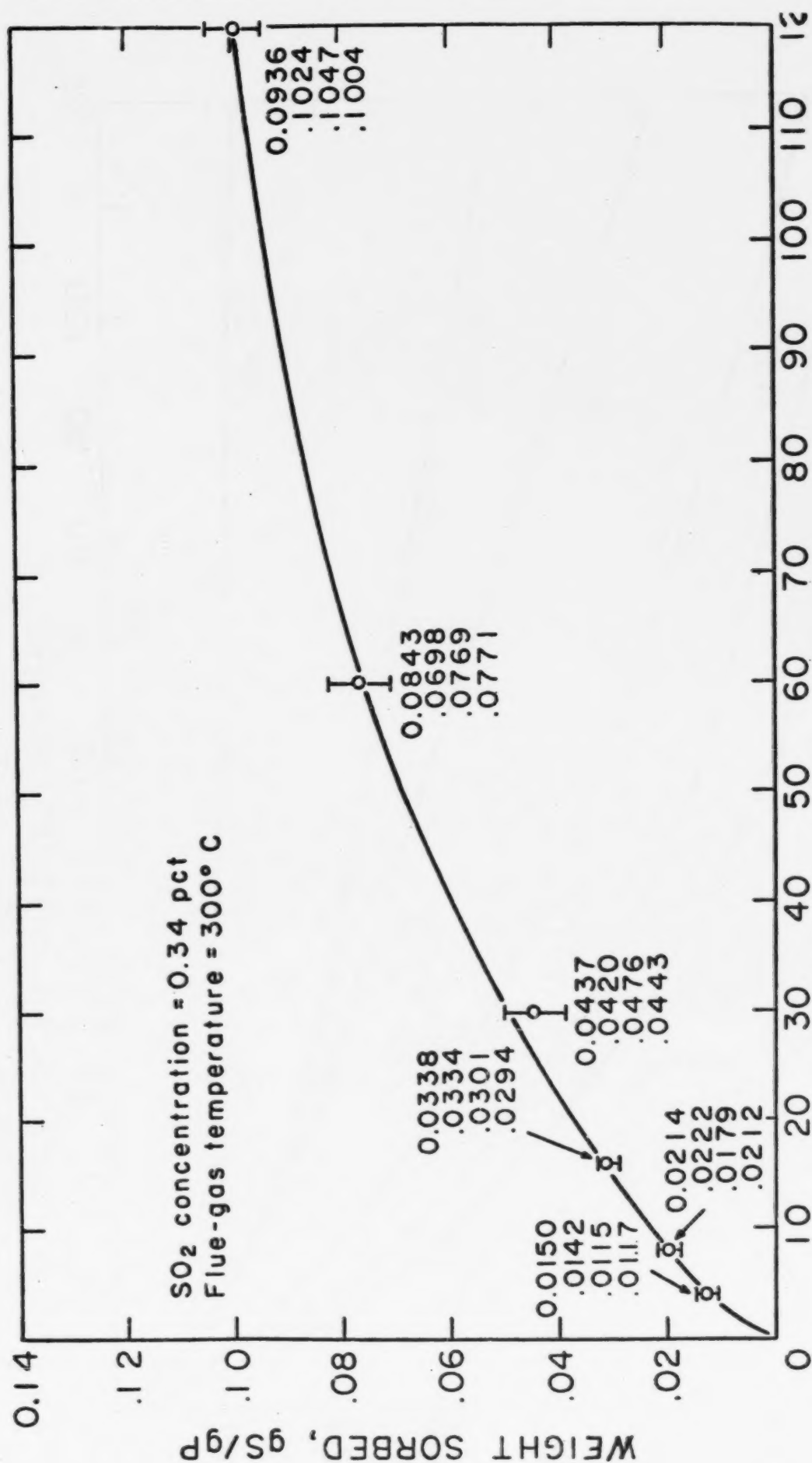


FIGURE 19 - Reproducibility of Sulfur Loading
on Grace Alkalized-Alumina.

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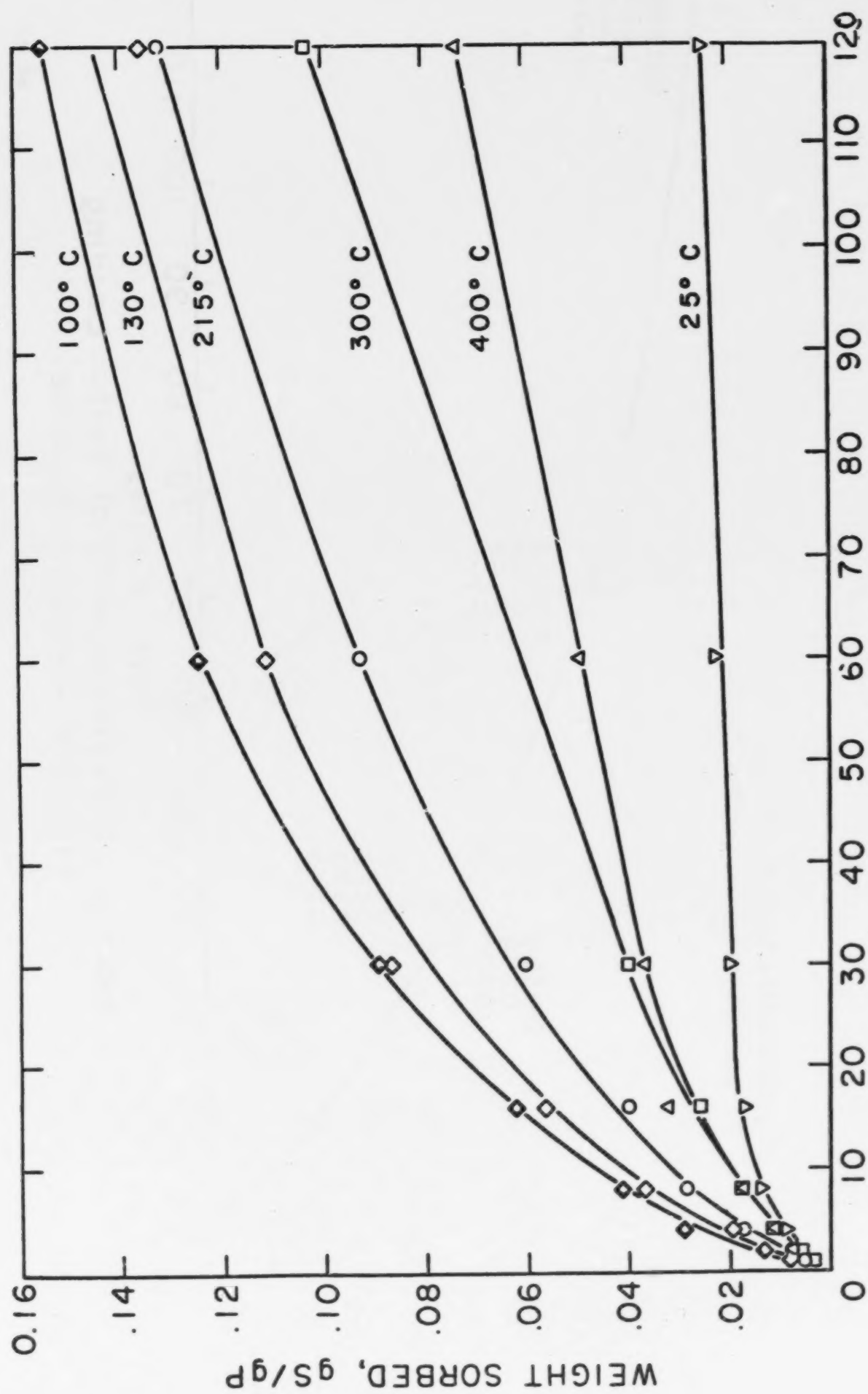


FIGURE 20 .-Effect of Temperature on Sulfur Loading in 0.34 percent SO_2 .

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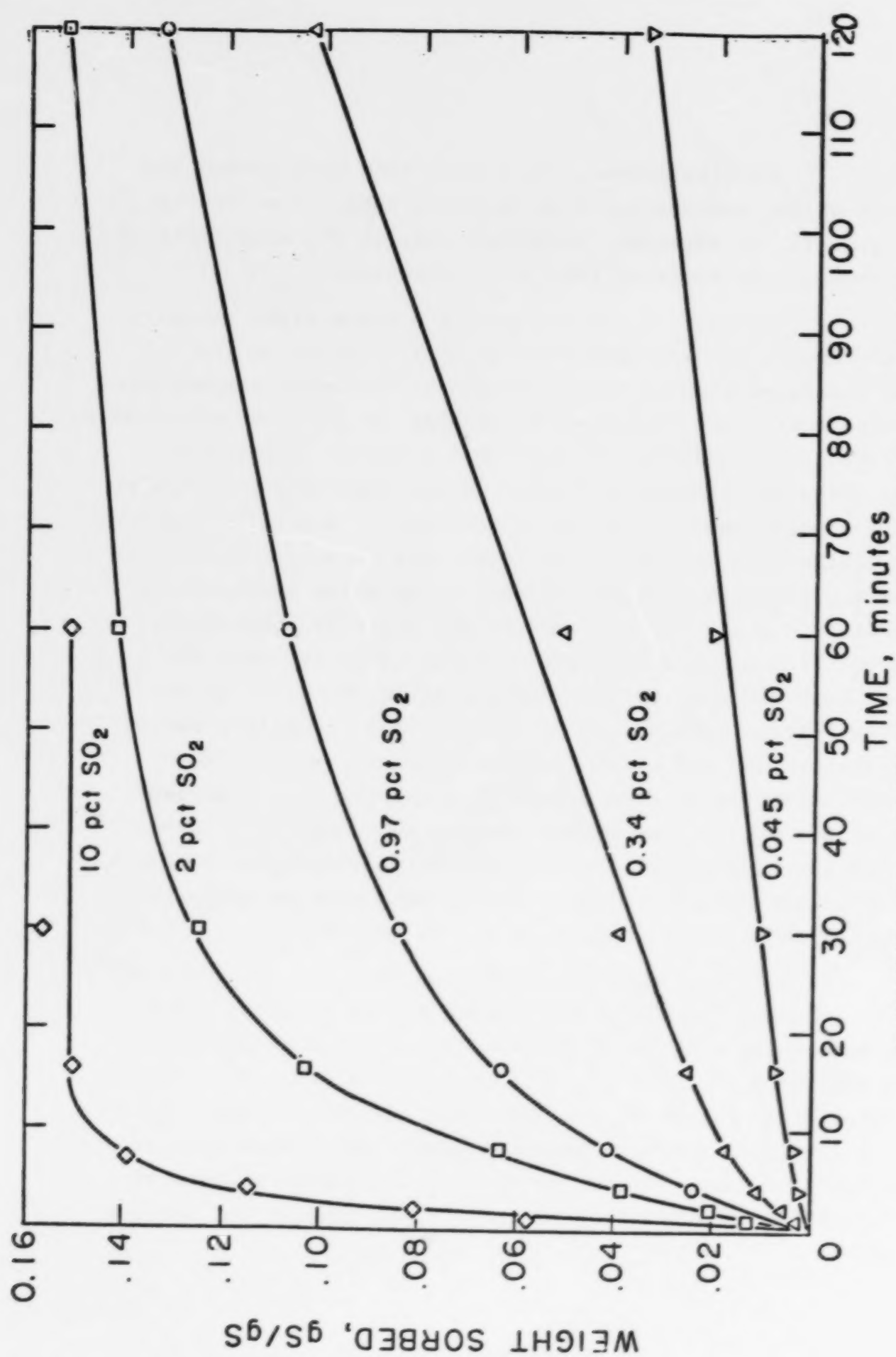


FIGURE 21 -Effect of SO_2 Gas Concentration
on Pellet Loading at 300°C .

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In like manner, the Albany test work showed the effects of SO_2 concentration on sorption rate. The results in Figure 21, as expected, indicated that as SO_2 concentration is increased the sorption rate also increases.

Because of the changes in surface area, porosity, and the amount of carbonate removed in activation of the Grace alkalized-alumina with hydrogen at different temperatures, sorption tests were conducted on samples of hydrogen activated at 300°, 600°, 700°, 750°, and 900°C for 4 hours. Results of these tests are plotted in Figure 22 and show that the initial sulfur loading was only slightly affected by activation temperature, while with longer contact times the effect of activation temperature became very pronounced. Activation temperatures between 600° and 700°C produced sulfur loads of about 0.028 gS/gP with 20 minutes flue gas contact, while at 300°C the pellet load was only 0.010 gS/gP and at 900°C, 0.017 gS/gP. The low sulfur loads at 300°C resulted from incomplete removal of the carbonate and water from the sorbent, while at 900°C the low sulfur loads were caused by sintering of the sorbent. Thus an activation temperature between 600° and 700°C is near optimum for high sulfur loading, which indicates that essentially all of the Dawsonite in the precipitate must be converted to sodium aluminate to obtain an active sorbent.

To determine if activation time had an effect on pellet loading with different contact times, sorption tests were made using samples of Grace alkalized-alumina that had been activated at 600°C for 2, 4, 6, and 8 hours. Test results are plotted in Figure 23 and show that the pellet loads obtained for given contact times are nearly equal with respect to activation time. Hence, an activation time of 2 hours at 600° to 650°C is sufficient to prepare the samples for optimum sorption.

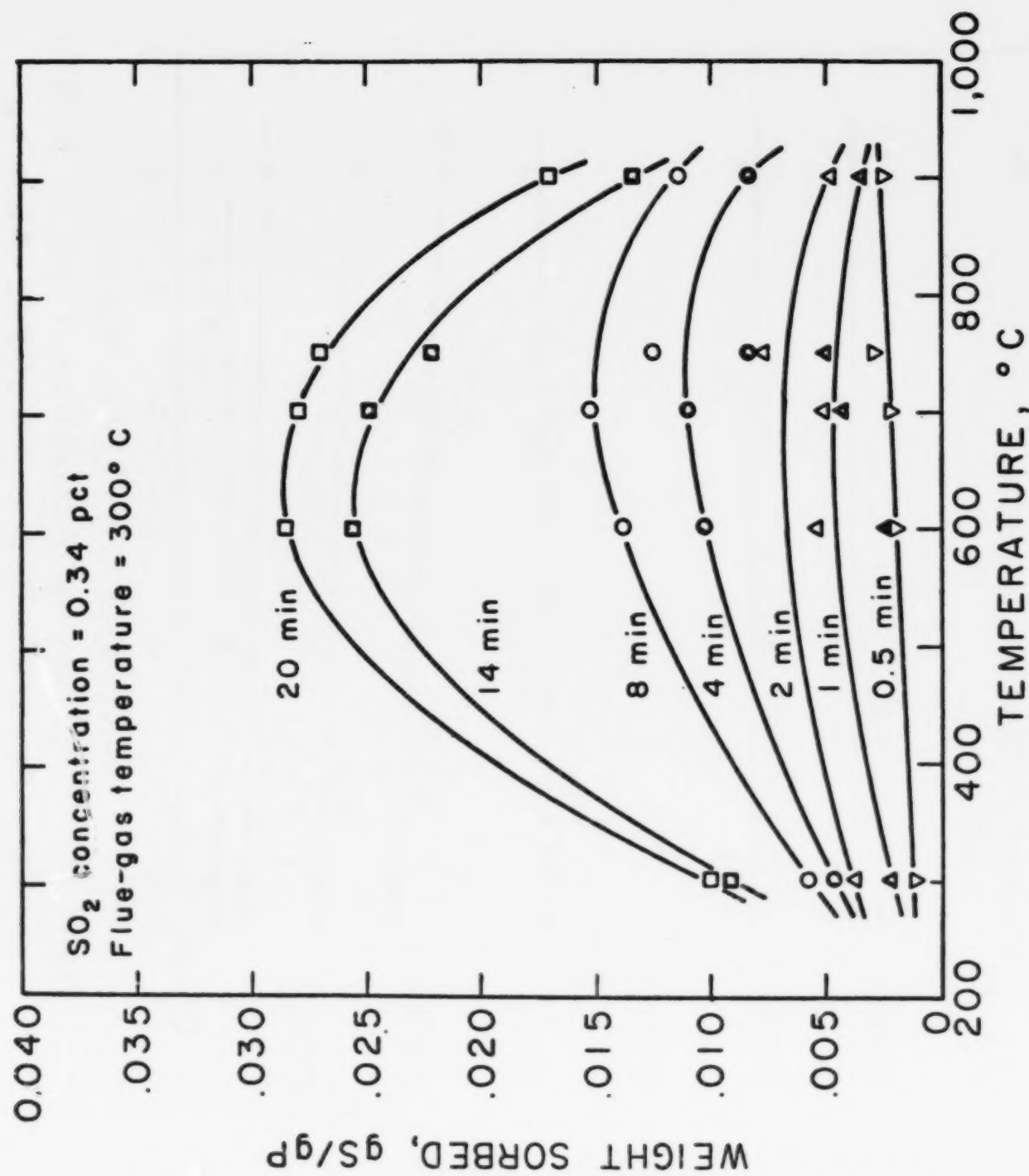


FIGURE 22 .-Effect of Activation Temperature
on SO₂ Sorption-Grace Alkalized-Alumina.

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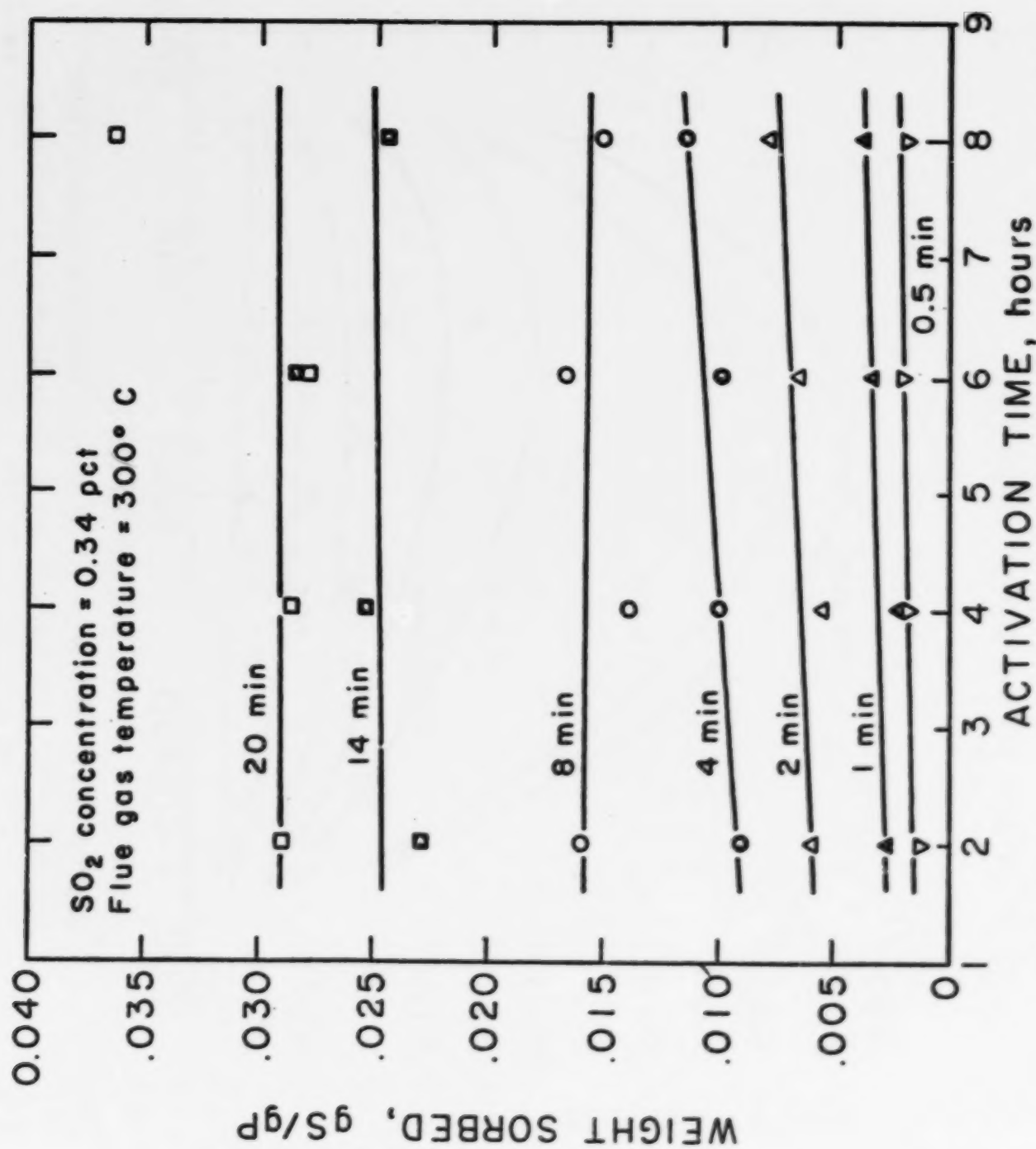


FIGURE 23 -Effect of Activation Time at 600° C
on SO₂ Sorption-Grace Alkalized-Alumina.

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When it became evident that nitrogen oxides (NO_x) played a major role in SO_2 sorption, tests were made to determine how the NO_x -free results would be affected. As shown in Figure 16 and Table 9, sorption rates increased by approximately 2 to 3.5-fold when nitrogen oxides were added to the flue gas. When the sorption temperature was lowered from 300°C to either 215° or 130°C , the sorption rates were reduced (e.g. by about 25% for each step) thus showing considerable difference from the results reported in Figure 20, wherein the 100 to 130°C sorption temperature in the absence of nitrogen oxides showed a significant increase in rates over the 300°C data.

Not only did the USBM-Albany study the various parameters which affected the sorption of SO_2 from flue gases containing nitrogen oxides, but they also provided the only extensive sorption data for tests of this type. These data are summarized in Table 10.

The USBM-Albany is also the prime researcher in the area of fluidized bed sorption. Their fluid bed sorption system test apparatus is shown schematically in Figure 24 and is operated in the following manner. The system is brought to temperature while the chromatograph and Leco titration units are being standardized. Grace No. 1 pellets are added to the sorption system to obtain the desired fluidized-bed depth. The sorption unit is allowed 30 minutes for the bed to equilibrate. To begin the run the SO_2 and NO flows are started and the pellet feeder is set to feed 10 g/min of pellets to the system. Gas analyses are obtained at 10 minute intervals and a representative sample (loaded pellets) is removed from the underflow for sulfur analysis every 30 minutes. The underflow of the system is sent to a regeneration unit and is recycled as feed to the sorber after sulfur removal.

TABLE 9 - Comparison of Sorption Rates With and Without NO_x 2)

Sorption temp., °C	SO ₂ conc., percent	Pellet load, gS/gP	Time required to load, minutes		Sorption Rate, 10 ⁻⁵ gS/gP/sec.		Sorption ratio with NO _x to without NO _x
			Without NO _x	With NO _x	Without NO _x	With NO _x	
300	0.045	0.10	4701)	1811)	0.35	0.92	2.6
300	0.34	0.10	116	30	1.44	5.05	3.5
300	1.0	0.10	48	16	3.47	10.4	3.0
300	2.0	0.10	16	5	10.4	33.3	3.2
300	10.0	0.10	2.5	2.5	66.6	66.6	---
300	0.045	0.05	1851)	82	0.45	1.02	2.3
300	0.34	0.05	31	10.5	2.69	7.94	3.0
300	1.0	0.05	12	6.0	6.94	13.9	2.0
300	2.0	0.05	5.0	1.75	16.7	47.8	2.9
300	10.0	0.05	1.25	1.25	66.6	66.6	---
215	0.34	0.10	71	42	2.35	3.97	1.7
215	0.34	0.05	20	14	4.17	5.95	1.4
130	0.34	0.10	47	62	3.55	2.69	0.76
130	0.34	0.05	15	19	5.56	4.38	0.78

1) Projected times required to obtain load.

2) From USBM-Albany, Yearly Report, June 30, 1969.

TABLE 10

EFFECT OF NO₂ AND NO ON SO₂ SORPTION RATE - GRACE ALKALIZED ALUMINA¹⁾

NITROGEN OXIDE CONCENTRATE APPROXIMATE PPM	NITROGEN -OXYGEN ADDED	SO ₂ CONCENTRATE PERCENT	TEMP. °C	4	8	CONTACT TIME, MINUTES			
						16	30	60	120
						WEIGHT SORBED, gs/gp			
300	NO ₂	.34	300	0.0177	0.0369	0.0484	0.0476	0.1006	0.1459
500	NO ₂	.34	300	.0122	.0205	.0379	.0558	.0923	.1311
1000	NO ₂	.34	300	.0126	.0227	.0334	.0672	.1040	----
150	NO ₂	.34	300	.0135	.0206	.0428	.0650	.0993	.1395
300	NO ₂	.34	500	.0221	.0224	.0372	.0553	.0618	.0800
300	NO ₂	.34	215	.0130	.0225	.0425	.0650	.0928	.1292
300	NO ₂	.34	130	.0135	.0226	.0429	.0610	.0844	.1117
500	NO	.34	300	.0175	.0357	.0646	.0955	.1302	.1524
500	NO	.34	215	.0178	.0296	.0517	.0751	.1161	.1257
500	NO	.34	130	.0180	.0336	.0387	.0643	.1080	.1262

 1) From USBM-Albany, Quarterly Report, June 30, 1968, pp BM-44

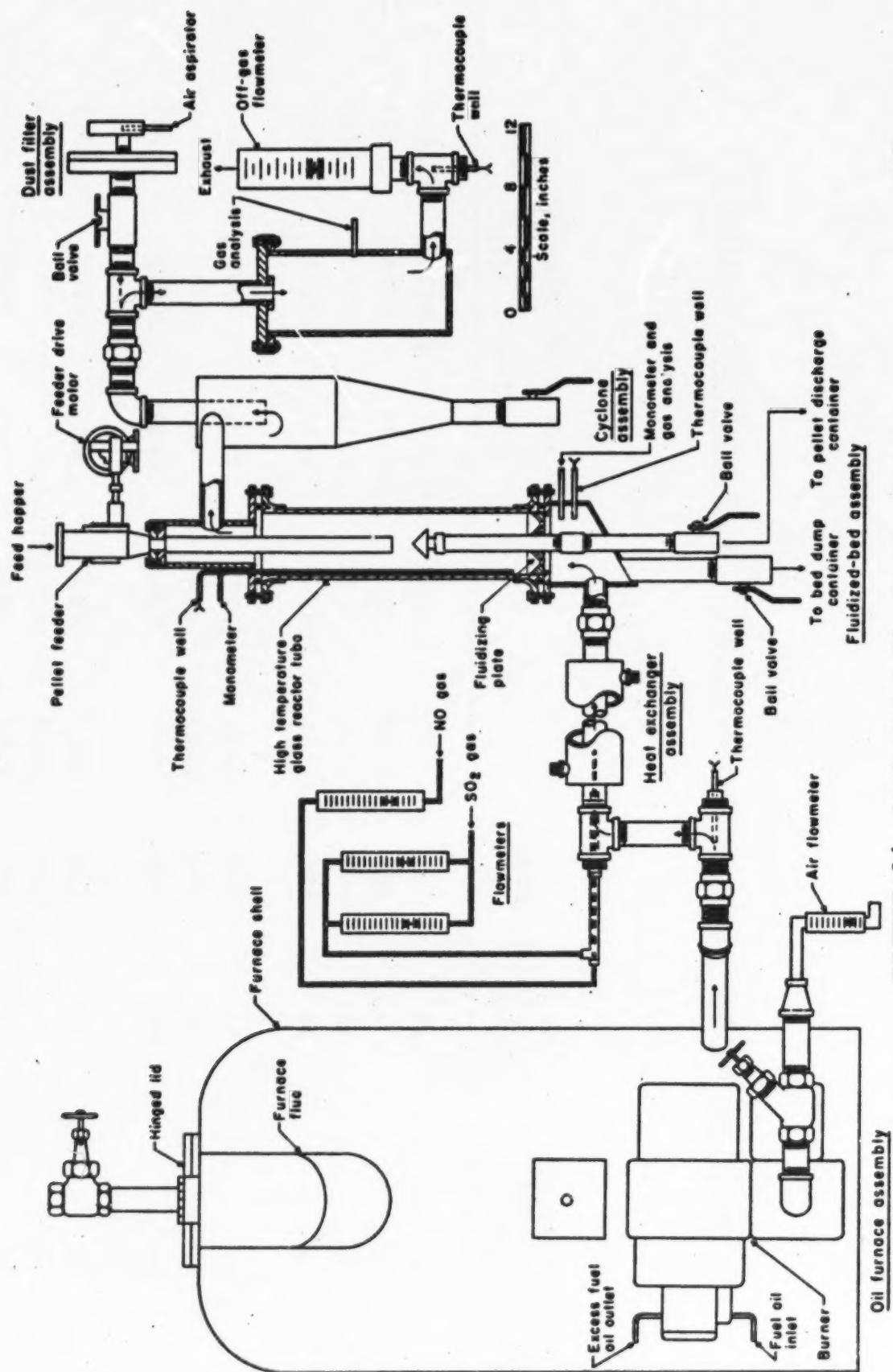


FIGURE 24.-Fluidized-Bed SO_2 Sorption System.

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Using this apparatus a series of sorption runs were made using a typical power plant flue gas as feed. The initial series of 17 one day tests shown in Tables 11 and 12 indicated that on the average 78% of the inlet SO₂ was removed. Furthermore, if runs 7, 11, 13, and 14 are discounted, due to the high sorbent sulfur loadings which are far in excess of the loadings used in the commercial design, the average SO₂ removal becomes 85%.

The encouraging results obtained in the one day test series were then confirmed by an extended sorption run of 100 hours. The data obtained during this run are shown in Tables 13 and 14. For this extended run, the average removal of SO₂ was 90.2%. The conditions used during this run are comparable to the proposed commercial design conditions; therefore, the present commercial fluid bed sorption scheme which is designed to remove 90% of the flue gas SO₂ appears to be feasible. The other data presented provide a basis for determining the commercial bed's physical properties (e.g., density, expansion, pressure drop, etc.). The present design was made before these data were available but there does not appear to be any large discrepancies between the assumed and the experimental values so no adjustments to reactor design are planned at the present time.

(3) USBM-Bruceton

USBM-Bruceton discovered the alkalized alumina sorbent and did the original experimental work using first a bench-scale fixed bed apparatus and later a downflow reactor. The data from the bench-scale fixed bed unit were used as a basis for designing the first pilot plant which used a downflow reactor. The following discussion is taken essentially verbatim from a Bruceton report.

TABLE 11 - Fluidized-Bed (Sorption System) Tests of One-Day Duration

Run No.	Run time, hrs.	Velocity, ft/sec	Height, inches	Expansion, inches	Weight, grams	Density, g/cc	Analysis, % sulfur	Temp., °C	ΔP, inches H ₂ O	Pellet bulk density, g/cc
3	5.5	-	5 ^a	-	574	.56	4.5	340	4	-
4	4.0	-	5 ^a	-	573	.56	4.8	340	3-1/4	-
5	5.0	-	5 ^a	-	553	.54	7.4	340	3-1/2	-
6	5.0	-	5 ^a	-	650	.63	8.5	340	4	-
7	5.2	-	5 ^a	-	713	.69	9.9	340	4	-
8	5.0	-	7.5 ^a	-	677	.44	4.9	340	4	-
9	5.0	2.4	7.5 ^a	-	968	.63	5.7	325	4-3/4	-
10	5.0	2.4	7.5 ^a	-	1125	.73	7.1	350	4-3/4	-
11 ^b	5.0	3.4	7.5 ^a	1-1/4	1458	.84	10.1	375	7-1/2	-
12	5.0	3.6	5.3	-	804	.74	8.4	330	4-1/2	-
13	5.1	3.6	5.3	1-3/4	730	.67	10.9	335	4-1/4	.99
14	5.0	2.9	5.5	1-1/2	854	.75	10.4	315	4-5/8	1.02
15	5.0	2.6	4.3	7/8	645	.73	5.1	336	3-3/4	.83
16	5.0	3.6	3.5	3/4	605	.84	8.2	355	3-1/2	.92
17 ^c	5.0	3.6	6.0	1	738	.60	5.6	326	4-1/2	.80
18 ^d	5.1	3.5	6.0	3/4	788	.64	6.6	324	4-1/2	.80
19 ^e	4.0	2.6	5.3	-	800	.72	-	309	4-1/8	.78

Run No.	Oxylene Product, g/hr.	Throughput, %	Feed gas, % SO ₂	Feed gas, % SO ₂	Off gas, % SO ₂	Gas analysis, % sorbed	Pellet and flowmeter, % sorbed
3	14	0.4	0.5	-	0.12	0.02	83
4	5	0.2	0.2	-	0.13	0.02	85
5	17	0.6	0.6	-	0.22	0.04	84
6	14	0.4	0.5	-	0.38	0.12	80
7	13	0.4	0.5	-	0.45	0.19	58
8	27	0.8	0.9	-	0.14	0.02	85
9	17	0.4	0.6	0.20	0.20	< .01	94
10	14	0.2	0.5	0.32	0.28	< .01	95
11 ^b	16	0.2	0.5	0.38	0.38	0.17	55
12	40	0.9	1.4	0.34	0.33	0.09	73
13	31	0.8	1.1	0.47	0.44	0.22	50
14	19	0.4	0.7	0.57	0.64	0.21	67
15	10	0.3	0.3	0.20	0.20	< .01	95
16	17	0.6	0.6	0.35	0.39	0.12	69
17 ^c	164	4.4	5.0	0.21	0.24	0.02	92
18 ^d	148	3.7	5.1	0.22	0.25	0.03	88
19 ^e	64	2.0	2.2	0.24	0.25	0.02	92

- ^a New Grace No. 1 activated at Albany
- ^b Superficial space velocity at temperature
- ^c ΔP represents pressure drop across fluidizing plate and pellet bed
- ^d Percent of bed weight
- ^e Percent of feed rate
- ^f Nominal height
- ^g Bed segregated because of insufficient fluidization velocity.
- ^h Concentration calculated from exit gas velocity and SO₂ input
- ⁱ Concentration by gas chromatograph analysis
- ^j Percent sorbed based on total throughput.

TABLE 12 - Evaluation of fluid-bed tests of one-day duration, for steady-state

Sorption	Run No.							
	3	4	5	6	7	8	9	10
<u>Parameters fixed</u>								
Load in, w_0 , gS/gp	0.0096	0.0097	0.0148	0.0203	0.0261	0.0146	0.0170	0.0185
Feed rate, w , gp/min	9.4	9.7	10.1	9.8	9.5	10.6	10.4	10.0
Bed weight, W , gp	510.	504.	451.	512.	536.	504.	830.	926.
SO ₂ feed, s , gS/min	0.45	0.41	0.72	1.15	1.47	0.47	0.47	0.74
SO ₂ concentration, y_0	0.0012	0.0013	0.0022	0.0038	0.0045	0.0014	0.0020	0.0028
<u>Results</u>								
Load out, $\bar{u}$, gS/gp	0.057	0.051	0.077	0.111	0.129	0.055	0.059	0.081
SO ₂ remaining, y_X/y_0 (gas analysis)	0.18	0.14	0.16	0.32	0.42	0.15	0.07	0.05
SO ₂ remaining, y_X/y_0 (pellet analysis)	0.04	0.02	0.13	0.23	0.34	0.09	0.08	0.15
<u>Calculated</u>								
Load out, $\bar{u}$, gS/gp	0.049	0.048	0.068	0.098	0.111	0.056	0.071	0.095
SO ₂ remaining, y_X/y_0	0.15	0.09	0.26	0.34	0.45	0.07	0.19	0.03
<u>Regeneration</u>								
<u>Parameters fixed</u>								
Load in, w_0 , gS/gp	0.056	0.051	0.077	0.111	0.129	0.055	0.059	0.081
Feed rate, w , gp/min	7.3	8.9	9.3	8.2	9.0	8.4	9.4	10.0
Bed weight, W , gp	367.		361.	392.	416.	479.	410.	347.
<u>Results</u>								
Load out, $\bar{u}$, gS/gp	0.013	0.015	0.020	0.023	0.029	0.015	0.017	0.021
Rate constant, K , min ⁻¹	0.067		0.075	0.080	0.077	0.046	0.056	0.082

Sorption	Run No.							
	12	13	14	15	16	17	18	19
<u>Parameters fixed</u>								
Load in, w_0 , gS/gp	0.0256	0.0292	0.0327	0.014	0.022	0.009	0.008	0.013
Feed rate, w , gp/min	11.1	9.6	9.8	13.4	11.2	11.5	9.9	9.1
Bed weight, W , gp	635.	531.	635.	563.	482.	635.	658.	648.
SO ₂ feed, s , gS/min	1.18	1.65	1.65	0.49	1.17	0.73	0.74	0.63
SO ₂ concentration, y_0	0.0033	0.0044	0.0064	0.0020	0.0039	0.0024	0.0025	0.0024
<u>Results</u>								
Load out, $\bar{u}$, gS/gp	0.100	0.129	0.136	0.054	0.095	0.060	0.064	0.067
SO ₂ remaining, y_X/y_0 (gas analysis)	0.27	0.50	0.33	0.07	0.31	0.10	0.10	0.07
SO ₂ remaining, y_X/y_0 (pellet analysis)	0.30	0.42	0.39	0.10	0.30	0.21	0.25	0.23
<u>Calculated</u>								
Load out, $\bar{u}$, gS/gp	0.098	0.112	0.126	0.053	0.092	0.069	0.077	0.080
SO ₂ remaining, y_X/y_0	0.32	0.52	0.45	0.07	0.33	0.06	0.08	0.04
<u>Regeneration</u>								
<u>Parameters fixed</u>								
Load in, w_0 , gS/gp	0.099	0.124	0.135	0.055	0.096	0.052	0.061	0.067
Feed rate, w , gp/min	9.9	10.6	10.5	11.5	10.0	9.7	9.0	9.3
Bed weight, W , gp	432.	361.	305.	632.	502.	580.	557.	347.
<u>Results</u>								
Load out, $\bar{u}$, gS/gp	0.027	0.033	0.036	0.014	0.024	0.009	0.009	0.015
Rate constant, K , min ⁻¹	0.064	0.081	0.096	0.054	0.060	0.076	0.092	0.094

TABLE 13 - Fluidized-Bed (Sorption System) Test for 100 Hours

Shift No.	Time, hours	Velocity ¹ , ft/sec	Height, inches	Weight ² , grams	Density, g/cc	Analysis ³ , % S	Temp., °C	ΔP ⁴ , inches H ₂ O	Pellet Feed Rate, g/min	Gas/gp x100	Cyclone Product		Feed Gas ⁶ SO ₂ , %	Feed Gas ⁶ SO ₂ , %	Off Gas ⁷ SO ₂ , %	SO ₂ , cc/min	Gas analysis, % sorbed	
											grams	%/hr throughput ⁵						
1-1	2.5	3.3	6.3	890	.69	3.9	322	4-5/8	9.8	4.4	60	2.7	4.1	0.22	0.27	0.02	500	-
1-2	4.0	3.3	6.3	915	.71	6.6	329	4-3/4	9.2	8.0	98	2.7	4.4	0.22	0.27	0.02	500	93
2-1	4.0	3.3	6.3	915	.71	6.2	329	4-3/4	10.8	7.3	94	2.6	3.6	0.23	0.28	0.02	508	93
2-2	4.0	3.3	6.3	890	.69	6.8	324	4-5/8	10.5	8.1	94	2.6	3.7	0.23	0.28	0.02	508	93
3-1	4.0	2.8	6.8	1060	.76	5.9	330	5-1/4	9.0	6.9	36	0.8	1.7	0.23	0.26	0.01	440	-
3-2	4.0	3.1	6.8	1170	.84	6.2	333	5-3/4	10.2	7.5	36	0.8	1.5	0.21	0.24	0.01	440	96
4-1	4.0	3.3	6.3	860	.66	7.4	333	4-1/2	9.8	9.2	55	1.6	2.3	0.20	0.22	0.02	444	91
4-2	4.0	3.2	6.3	800	.62	7.0	326	4-1/4	10.0	8.5	56	1.8	2.3	0.20	-	-	444	-
5-1	4.0	3.2	5.8	715	.60	5.3	324	3-7/8	9.5	6.1	45	1.6	2.0	0.17	0.20	0.01	368	95
5-2	4.0	3.2	5.8	685	.57	5.2	322	3-3/4	10.1	5.9	46	1.7	1.9	0.17	0.20	0.02	368	90
6-1	4.0	3.2	5.5	685	.60	5.2	320	3-3/4	10.8	6.1	62	2.3	2.4	0.17	0.20	0.02	368	90
6-2	4.0	3.2	5.5	685	.60	5.1	319	3-3/4	10.8	5.9	63	2.3	2.4	0.17	0.21	0.02	368	91
7-1	1.5	-	-	715	-	6.4	326	4	10.2	7.4	18	1.7	2.0	-	0.34	0.08	872	-
7-2	3.5	3.6	-	745	-	8.9	324	4-1/8	9.4	11.5	44	1.7	2.2	0.36	0.41	0.14	872	66
Bed	-	-	-	666	-	8.1	-	-	-	-	-	-	-	-	-	-	-	-
8-1	2.5	3.2	5.5	685	.60	4.5	310	3-3/4	20.2	4.9	58	3.4	1.9	0.31	0.40	0.03	662	-
8-2	5.5	3.2	5.5	715	.63	5.4	320	3-7/8	20.4	6.2	128	3.3	1.9	0.32	0.37	0.04	692	89
9-1	4.0	3.2	5.8	685	.57	6.5	322	3-3/4	16.3	7.7	56	2.0	1.4	0.32	0.37	0.04	692	89
9-2	4.0	3.2	5.8	685	.57	7.0	324	3-3/4	15.3	8.5	57	2.1	1.6	0.32	0.37	0.05	692	87
10-1	4.0	3.2	-	685	-	5.5	333	3-3/4	13.8	6.4	51	1.9	1.5	0.21	0.24	0.03	444	88
10-2	4.0	3.2	-	655	-	4.9	329	3-5/8	14.6	5.7	52	2.0	1.5	0.21	0.24	0.02	444	92
11-1	4.0	2.7	5.5	715	.63	4.8	309	3-3/4	15.7	5.4	41	1.4	1.1	0.23	0.26	0.02	440	92
11-2	4.0	2.7	5.5	715	.63	5.0	312	3-3/4	14.3	5.8	42	1.5	1.2	0.23	0.26	0.02	440	92
12-1	4.0	2.6	5.5	715	.63	5.8	317	3-3/4	9.9	6.9	30	1.0	1.3	0.23	0.27	0.02	440	93
12-2	4.0	2.8	5.5	715	.63	6.5	319	3-3/4	10.0	7.8	31	1.1	1.3	0.23	0.27	0.02	440	93
13-1	3.5	2.8	6.3	775	.60	6.6	319	4	9.7	8.0	22	0.8	1.1	0.23	0.27	0.03	431	89
13-2	3.5	2.8	6.3	775	.60	6.9	319	4	9.5	8.3	22	0.8	1.1	0.23	0.27	0.02	431	93
Bed	-	-	-	782	.60	6.6	-	-	-	-	-	-	-	-	-	-	-	-

¹ Superficial space velocity at temperature

² Bed weights were estimated from bed pressure drop

³ Based on average sulfur analyses of pellet overflow

⁴ AP represents pressure drop across fluidizing plate and pellet bed

⁵ Grams sulfur per gram pellet

⁶ Percent of bed weight

⁷ Percent of feed rate

⁸ Concentration calculated from exit gas velocity and SO₂ input

⁹ Concentration by gas chromatography analyses

TABLE 14 - Evaluation of fluid-bed test for 100 hours, steady-state operation

Shift Number												
1-2	2-1	2-2	3-2	4-1	4-2	5-1	5-2	6-1	6-2	7-2		
Parameters fixed												
Load in, W_0 , gS/gp	0.009	0.010	0.012	0.012	0.013	0.013	0.009	0.009	0.009	0.010	0.013	
Feed rate, W , gp/min	9.2	10.8	10.5	10.2	9.8	10.0	9.5	10.1	10.8	10.8	9.4	
Bed weight, W , gp ¹	743.	751.	701.	936.	719.	642.	606.	576.	576.	576.	531.	
SO ₂ feed, s , gS/min	0.72	0.73	0.73	0.63	0.64	0.64	0.53	0.53	0.53	0.53	1.25	
SO ₂ concentration, Y_0	0.0027	0.0028	0.0028	0.0024	0.0022	0.0022	0.0020	0.0020	0.0020	0.0021	0.0041	
Results												
Load out, $\bar{v}$, gS/gp	0.080	0.073	0.081	0.075	0.092	0.085	0.061	0.059	0.061	0.059	0.115	
SO ₂ remaining, Y_R/Y_0 , (gas analysis)	0.07	0.07	0.08	0.06	0.10	-	0.07	0.09	0.08	0.08	0.34	
SO ₂ remaining, Y_R/Y_0 , (pellet analysis)	0.08	0.07	0.01	-0.03	-0.21	-0.13	0.06	0.04	-0.06	-0.01	0.23	
Calculated												
Load out, $\bar{v}$, gS/gp	0.085	0.080	0.081	0.081	0.077	0.074	0.065	0.062	0.059	0.060	0.100	
SO ₂ remaining, Y_R/Y_0	0.01	-0.04	0.01	-0.13	0.02	0.05	-0.01	0.00	-0.02	-0.03	0.34	
Regeneration												
Parameters fixed												
Load in, W_0 , gS/gp	0.072	0.074	0.081	0.071	0.093	0.086	0.062	0.059	0.059	0.059	0.112	
Feed rate, W , gp/min	10.0	9.7	10.2	9.7	9.4	8.7	9.9	10.2	10.3	10.1	9.8	
Bed weight, W , gp ¹	346.	346.	346.	346.	346.	346.	346.	346.	346.	346.	346.	
Results												
Load out, $\bar{v}$, gS/gp	0.010	0.011	0.015	0.012	0.013	0.014	0.011	0.011	0.010	0.010	0.014	
Rate constant, K , min ⁻¹	0.170	0.170	0.133	0.132	0.170	0.134	0.138	0.132	0.144	0.138	0.207	

Shift Number												
8-2	9-1	9-2	10-1	10-2	11-1	11-2	12-1	12-2	13-1	13-2		
Parameters fixed												
Load in, W_0 , gS/gp	0.015	0.016	0.019	0.015	0.013	0.014	0.013	0.015	0.017	0.015	0.016	
Feed rate, W , gp/min	20.4	16.3	15.3	13.8	14.6	15.7	14.3	9.9	10.0	9.7	9.3	
Bed weight, W , gp ¹	600.	553.	544.	574.	556.	635.	625.	607.	589.	635.	636.	
SO ₂ feed, s , gS/min	0.99	0.99	0.99	0.64	0.64	0.63	0.63	0.63	0.63	0.62	0.62	
SO ₂ concentration, Y_0	0.0037	0.0037	0.0037	0.0024	0.0024	0.0026	0.0026	0.0027	0.0027	0.0027	0.0037	
Results												
Load out, $\bar{v}$, gS/gp	0.062	0.077	0.085	0.064	0.057	0.054	0.058	0.069	0.078	0.080	0.083	
SO ₂ remaining, Y_R/Y_0 , (gas analysis)	0.10	0.12	0.15	0.10	0.09	0.06	0.07	0.08	0.08	0.10	0.09	
SO ₂ remaining, Y_R/Y_0 , (pellet analysis)	0.02	0.01	-0.01	-0.06	-0.01	-0.01	-0.01	0.15	0.03	-0.02	-0.04	
Calculated												
Load out, $\bar{v}$, gS/gp	0.064	0.072	0.076	0.061	0.057	0.058	0.061	0.078	0.078	0.080	0.081	
SO ₂ remaining, Y_R/Y_0	-0.01	0.09	0.12	0.00	-0.01	-0.11	-0.09	0.00	0.02	-0.02	-0.01	
Regeneration												
Parameters												
Load in, W_0 , gS/gp	0.062	0.076	0.084	0.068	0.057	0.054	0.058	0.064	0.077	0.080	0.083	
Feed rate, W , gp/min	20.3	15.1	15.5	14.6	14.4	14.6	14.2	10.2	10.3	9.7	9.7	
Bed weight, W , gp ¹	346.	346.	346.	346.	346.	346.	346.	346.	346.	346.	346.	
Results												
Load out, $\bar{v}$, gS/gp	0.015	0.016	0.019	0.016	0.013	0.014	0.014	0.015	0.017	0.016	0.016	
Rate constant, K , min ⁻¹	0.184	0.165	0.155	0.138	0.140	0.118	0.132	0.096	0.106	0.110	0.115	

¹ Bed weights were estimated from pressure drop across the bed.

¹ Bed weights were estimated from pressure drop across the bed.

"The pilot plant consisted of a small pulverized coal furnace to produce a flue gas of desired composition, an absorber with its accessory equipment, and a separate unit for regeneration. Gas and solids flows through the absorber were continuous. A flow sheet of the flue gas generation and absorption system is shown schematically in Figure 25.

The absorber shown in Figure 26 was fabricated of 316 stainless steel. It was 26 feet long and had an inside diameter of 1.6 inches. Thermocouples and gas sampling ports, 180 degrees apart, extended to the center of the absorber and were placed at 4 feet intervals along the length of the column. Two pneumatically operated slide valves could be closed simultaneously during absorber operation and the solids caught between them were isolated and measured to determine the solids holdup. Baffles were made of 4-mesh stainless steel screen welded onto a 1/8 inch rod. The baffle assembly could be inserted into the absorber or removed as desired.

An induced draft fan located downstream of the absorber provided the necessary draft for the passage of the flue gas through the absorber. Linear velocity of the gas through the absorber was 8 to 15 feet/sec in countercurrent operation and 20 to 23 feet/sec in the entrained flow used in some of the later experiments.

A pulverized coal furnace supplied 250 to 1,000 cubic feet of hot flue gas from the combustion of 1 to 4 pounds of coal per hour. The products of combustion flowed from the furnace to two cyclone separators, in which about 60 to 70 percent of the fly ash was removed, and then entered the bottom of the absorber. Solids leaving the absorber were collected in a scales hopper. When a sufficient quantity of spent absorbent was accumulated, the regenerator was charged

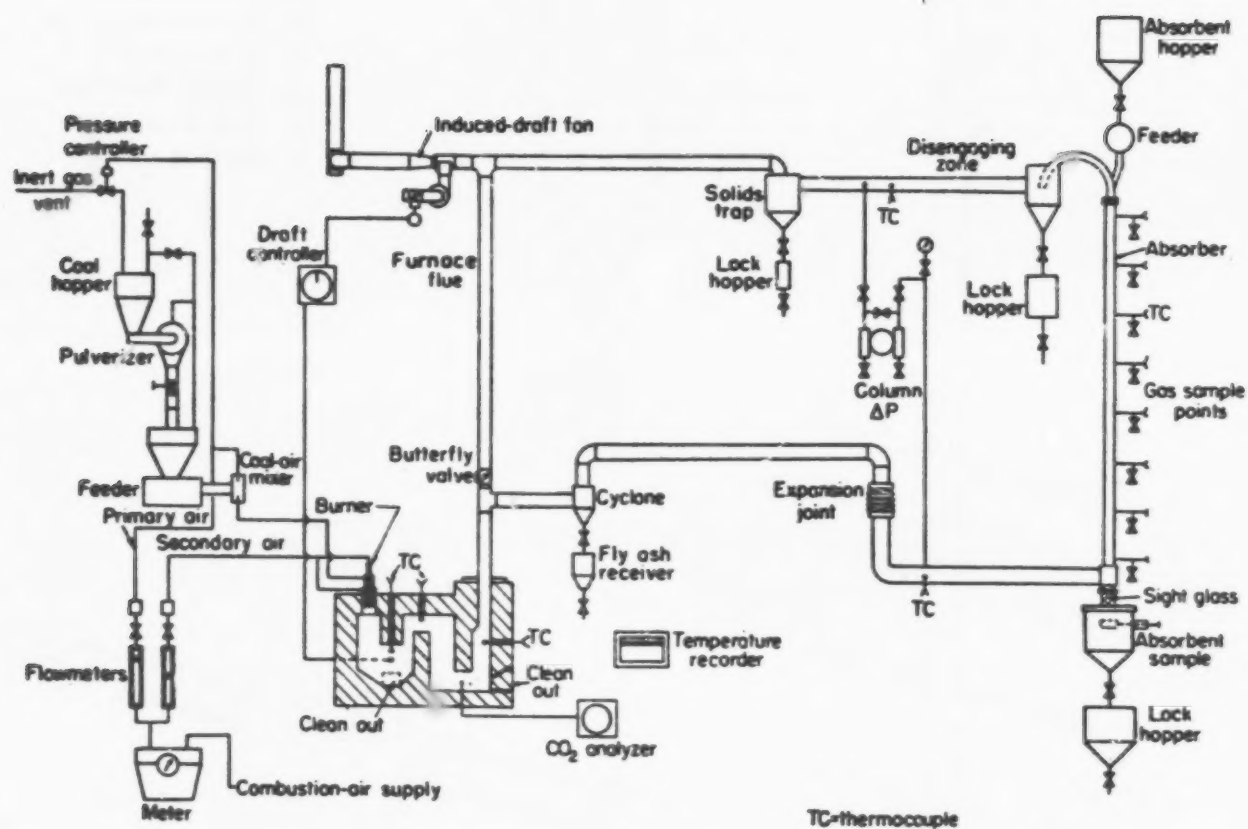


FIGURE 25 - Flue-Gas Generation and Sulfur Dioxide Absorption in Pilot-Plant Studies of the Alkalized Alumina Process.

¹²First work cited in footnote 10.

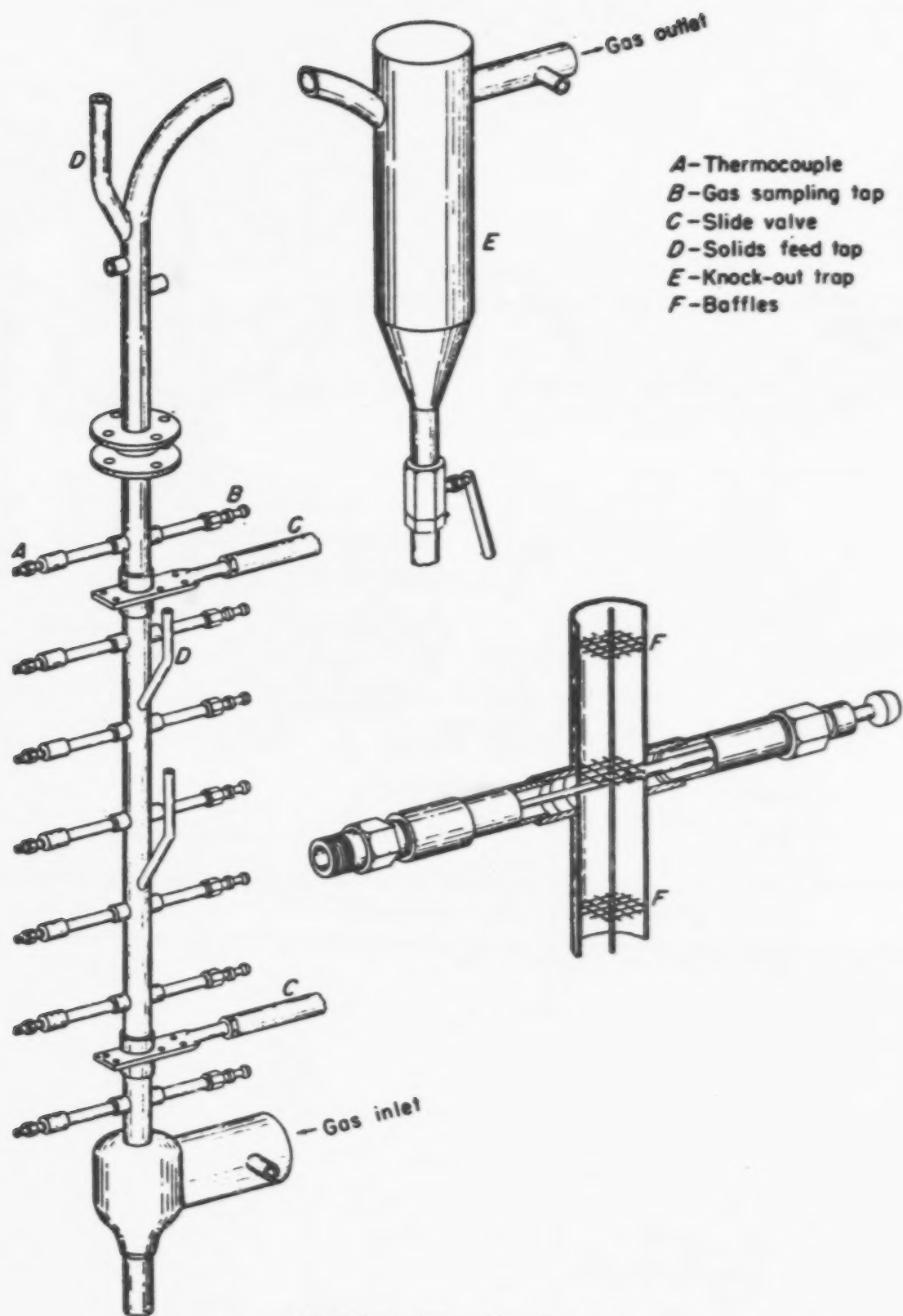


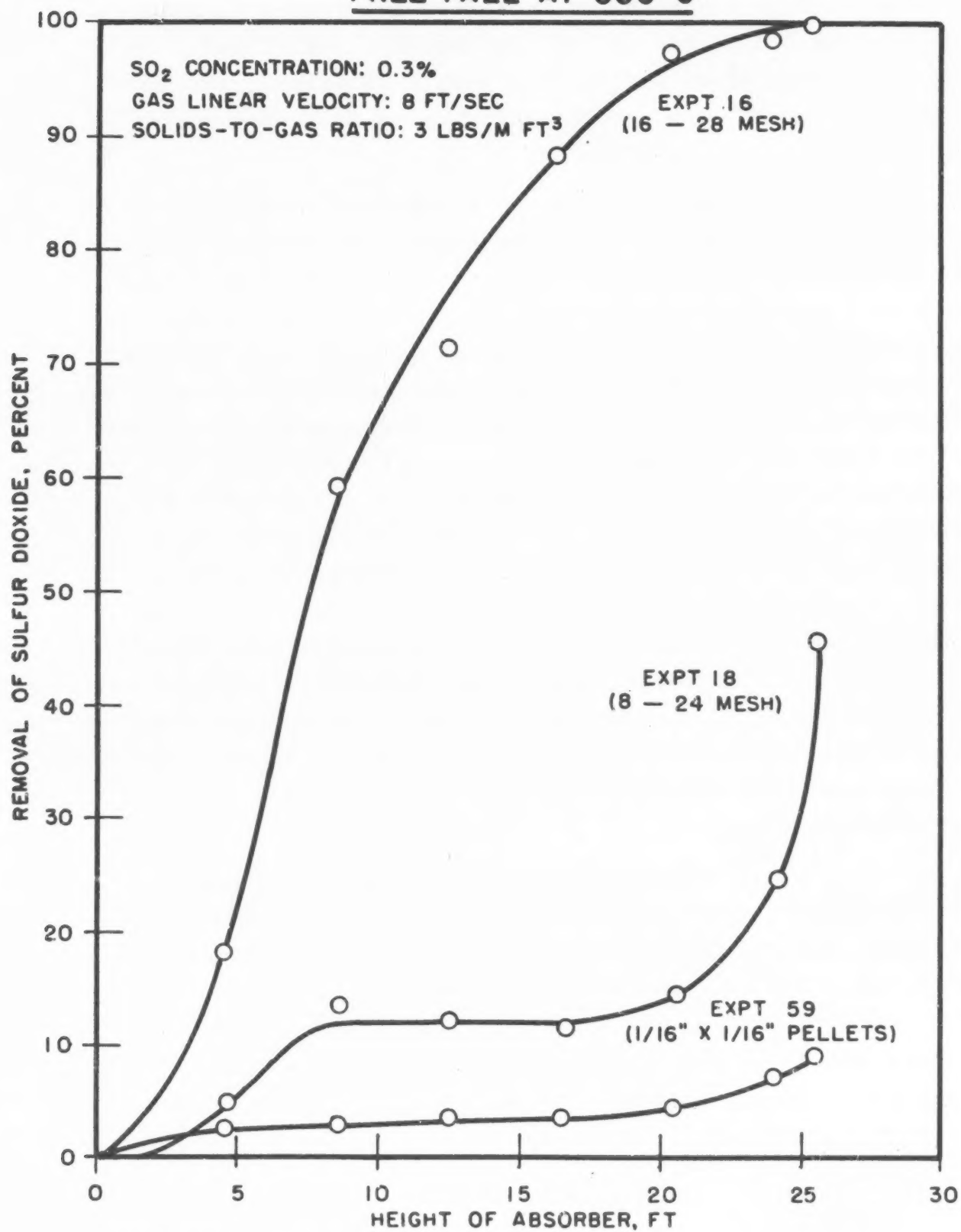
FIGURE 26 - Absorber.

and the fixed-bed of solids was regenerated with reducing gas. In countercurrent gas-solids operation the regenerated absorbent was fed to the top of the absorber. In tests with the solids entrained by the flue gas, a recycle stream of absorbent was returned to the absorber about 9 feet above the bottom of the column.

In the initial pilot plant work crushed alkalized alumina 8 to 24 and 16 to 28 mesh as well as the pelleted absorbent, 1/16" x 1/16", was tested in free fall at a feed rate of 3 pounds of absorbent per 1,000 actual cubic feet of the flue gas. The flue gas flowed at a velocity of 8 ft/sec countercurrent to the dropping solids. As shown in Figure 27, the smaller particles, 16 to 28 mesh, completely removed the sulfur dioxide. However, there was considerable loss of absorbent through carryover of the smaller particles. The absorption of the pellets was quite low in free fall even though the activity of the pellets when tested as a fixed bed in bench scale apparatus was equivalent to that of the crushed absorbent. Aerodynamically the crushed particles, containing platelets and slivers, are more readily buoyed by the upward flow of flue gas resulting in a greater residence time in the reactor and a higher degree of SO₂ absorption. The crushed particles also offer a higher surface area than the pelleted absorbent.

With increase in gas velocity, the buoyancy of the solids is increased resulting in a gain in solids holdup in the reactor and in the residence time. Figure 28 shows the effect of raising the gas velocity from 8 to 12 to 15 ft/sec upon the degree of SO₂ removal. Accompanying the greater pickup of SO₂ with higher gas velocities there is a greater loss of absorbent, as solids carryover, as the

FIGURE 27
REMOVAL OF SULFUR DIOXIDE WITH ALKALIZED ALUMINA
IN
FREE FALL AT 330°C



REFERENCE:
 USBM Bruceton Quarterly Report, pg. BM-13, (June 30, 1963).

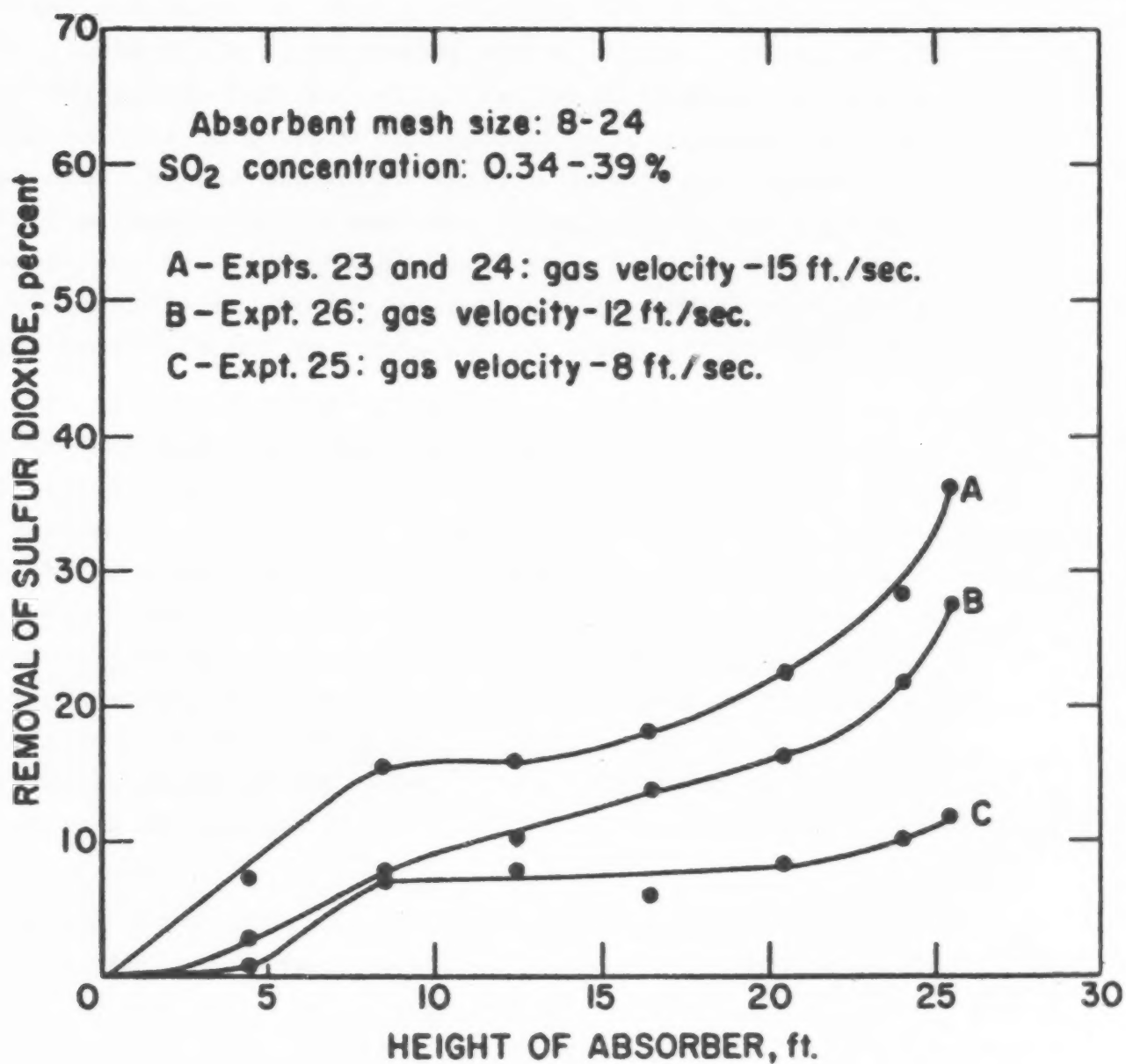


FIGURE 28 -Removal of sulfur dioxide as a function of liner gas velocity with regenerated alkalinized alumina at a solids-to-gas ratio of 3 lbs./M ft.³ of gas.

gas velocity is raised. In addition to this effect of carry-over the shape of the curves in Figure 28 indicates that much of the reactor length is not effective in SO_2 removal. There is greater removal of SO_2 at the bottom and top of the absorber. The fresh absorbent is injected at the top of the reactor where its freshly regenerated surface is conducive to rapid reaction with SO_2 . At the bottom of the reactor the entering flue gas contains the highest percentage of SO_2 and thus the greatest gas-driving force. Little removal of SO_2 is achieved in the midportion of the absorber, as shown by the flattened curves.

To achieve greater residence time, 100 stainless steel screens (4 openings to the inch) were spaced 3 inches apart in the absorber (Figure 26). Whereas in the free fall reactor the solids were in very dilute phase with a reactor residence of a few seconds, a 1-minute residence could now be obtained in the baffled reactor. The baffles by restricting the escape of the solid particles considerably reduced the loss in solids carryover. As shown in Figure 29, 64 percent of SO_2 was removed in the baffled reactor at a solids-to-gas ratio of 3 lb/1000 ft³ and a gas velocity of 12 ft/sec. In the absence of the baffles only 31 percent of the SO_2 was removed.

To increase the residence time still further the number of baffles was increased threefold. The screens of 4 mesh were placed 1 inch apart. At a gas velocity of 12 ft/sec, and a solids-to-gas ratio of 3 lb/1000 ft³, the residence time for the 1/16 inch pellets was 2 minutes and the removal of SO_2 was increased to 98 percent. The pressure drop across the 26 ft of absorber length was 6 inches of water.

In the previous tests, baffles of stainless steel screens were used to increase the solids residence

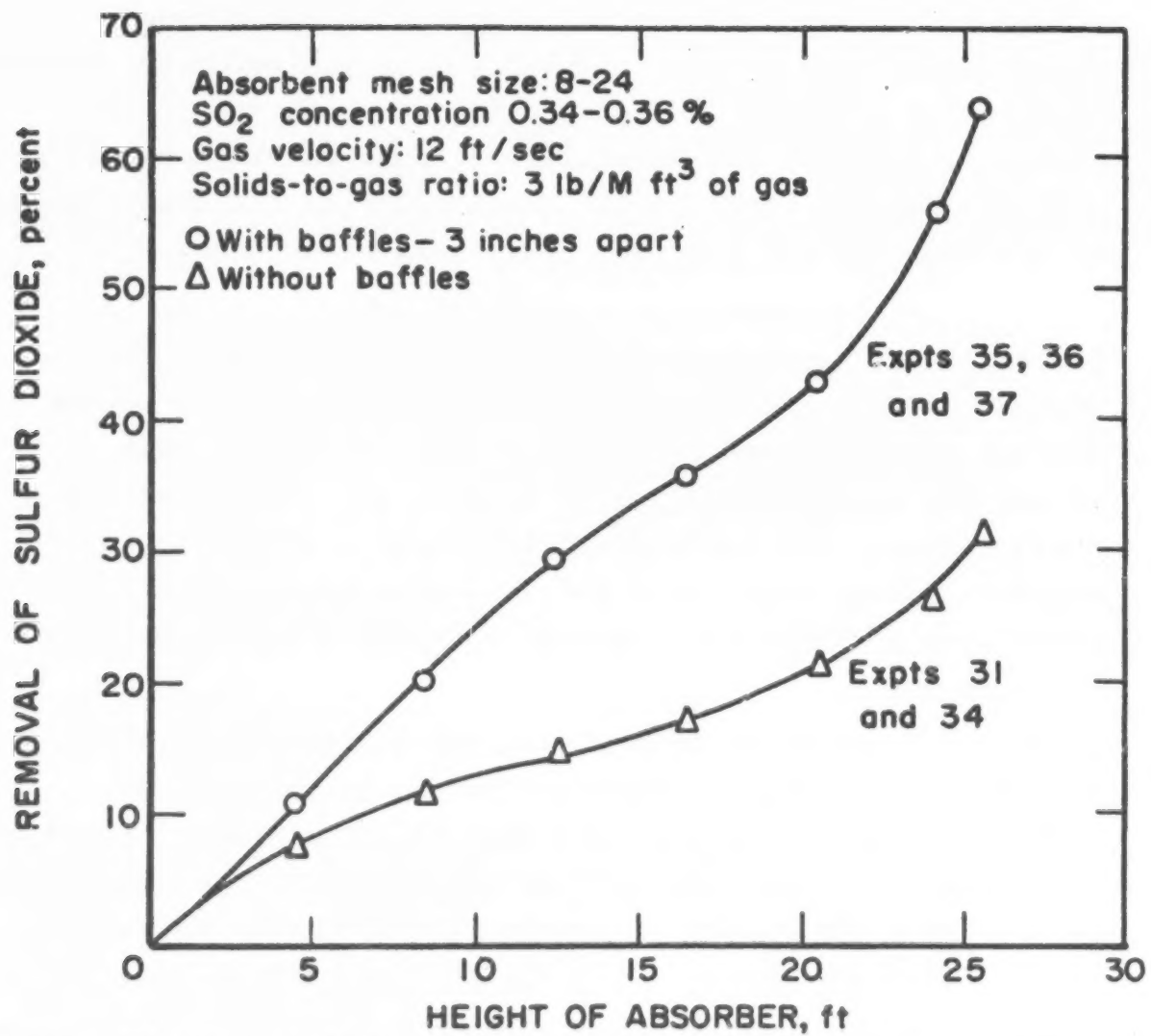


FIGURE 29 - Removal of Sulfur Dioxide With Alkalized Alumina in Presence and Absence of Baffles.

time. It was subsequently realized that these screens on an industrially sized reactor would be expensive, would limit the diameter of the absorber, and could cause excessive pressure drop through eventual blockage of the screens. It was observed that by increasing the flue gas velocity, solids entrainment occurs. If these solids are returned to the absorber, suitable solids-residence times can be achieved for high SO₂ removal, and greater flexibility in the usable range of gas velocity and absorbent size will be obtained.

Consequently, a recycle system as shown on Figure 30 was incorporated into the sorber design. The sorbent used in the testing of this system was of a poorer quality than had been used in the countercurrent tests, but it was the only preparation on hand at the time. Despite this drawback, the tests were sufficiently promising to warrant further study of a solids entrainment system. A comparison of these two types of sorption schemes is shown in Table 15.

As shown previously, the increase in residence time showed a marked improvement on the sorption of SO₂; therefore, it was hypothesized that if sorber height could be increased, to provide greater contact time, and the solids to gas ratio could also be increased, acceptable exit SO₂ levels would be obtained. To verify these assumptions the construction of a 55,000 cubic feet per hour pilot plant which incorporated these ideas was undertaken. Construction of this pilot plant which is depicted in the flow sheet in Figure 31, was completed in the first quarter of 1967.

The sorption section of the 55,000 CFH pilot plant was operated in the following manner. Coal is picked up at the coal pit (1) and pneumatically conveyed to a hopper (2).

TABLE 15 - Operating Conditions in Absorbing Sulfur Dioxide Under
Countercurrent Gas-Solids Flow Compared With Solids
Entrainment With Solids Recycle

Gas-solids contact	Countercurrent flow			Solids entrainment	
Test No.	1A	1B	1C	4A	6A
Gas velocity, ft/sec	12	13	14	23	23
Solids/gas, lb/M ft ³	3.0	2.8	2.4	2.2	2.4
SO ₂ , percent:					
In	0.33	0.27	0.32	0.36	0.36
Out	.23	.15	.09	.19	.18
Removal	30.3	44.4	71.9	47.2	50.0
Density, g/cm ³ :					
Charge	0.670	0.670	0.670	0.698	0.705
Bottoms	.726	.733	.766	.770	.769
Overhead	-	-	-	.748	.736
ΔP, inches of H ₂ O	-	4.7	7.5	2.2	1.8
Carryover; pct of feed, <20 mesh	0.02	0.04	0.08	-	-
Solids flow ratio:					
Overhead/bottoms	-	-	-	2.17	1.94
Reflux/fresh feed	-	-	-	10.4	10.4
Sulfur content, wt-pct:					
Charge	1.09	1.09	1.09	0.38	0.47
Spent bottoms	1.97	2.47	3.67	2.64	2.65
Spent overhead	-	-	-	2.80	2.38
Regeneration before run:					
Temperature, °F	1,210	1,210	1,210	1,200	1,220
Time, hr.	10	10	10	10	10
Space Velocity, hr ⁻¹	100	100	100	100	100
Gas	H ₂	H ₂	H ₂	H ₂ ·CO·CO ₂	H ₂ ·CO·CO ₂
				77 13 10	77 13 10

1) USBM-Bruceton - RI-7021, pg. 23.

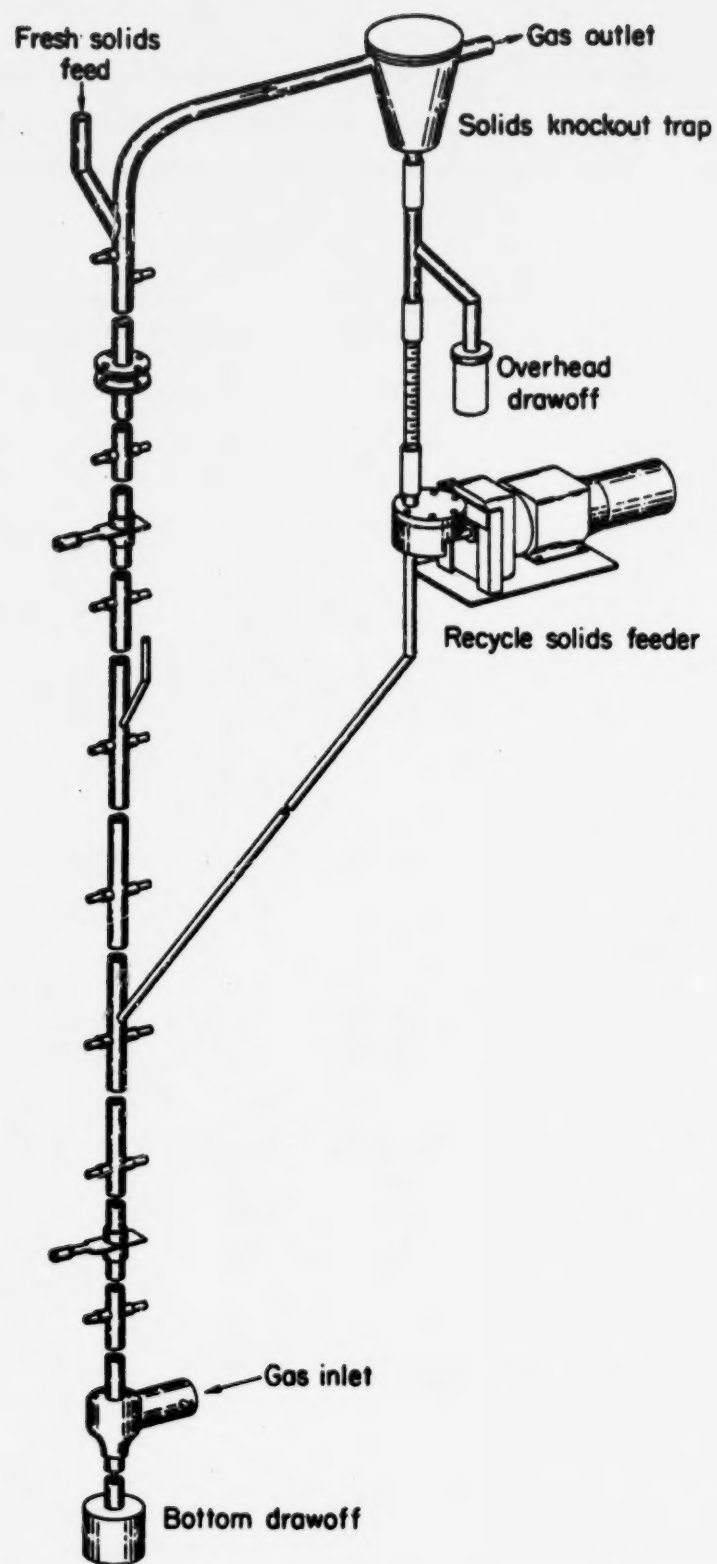


FIGURE 30--Absorber with solids recycle in alkylized alumina process.

12-10-64 L-8801

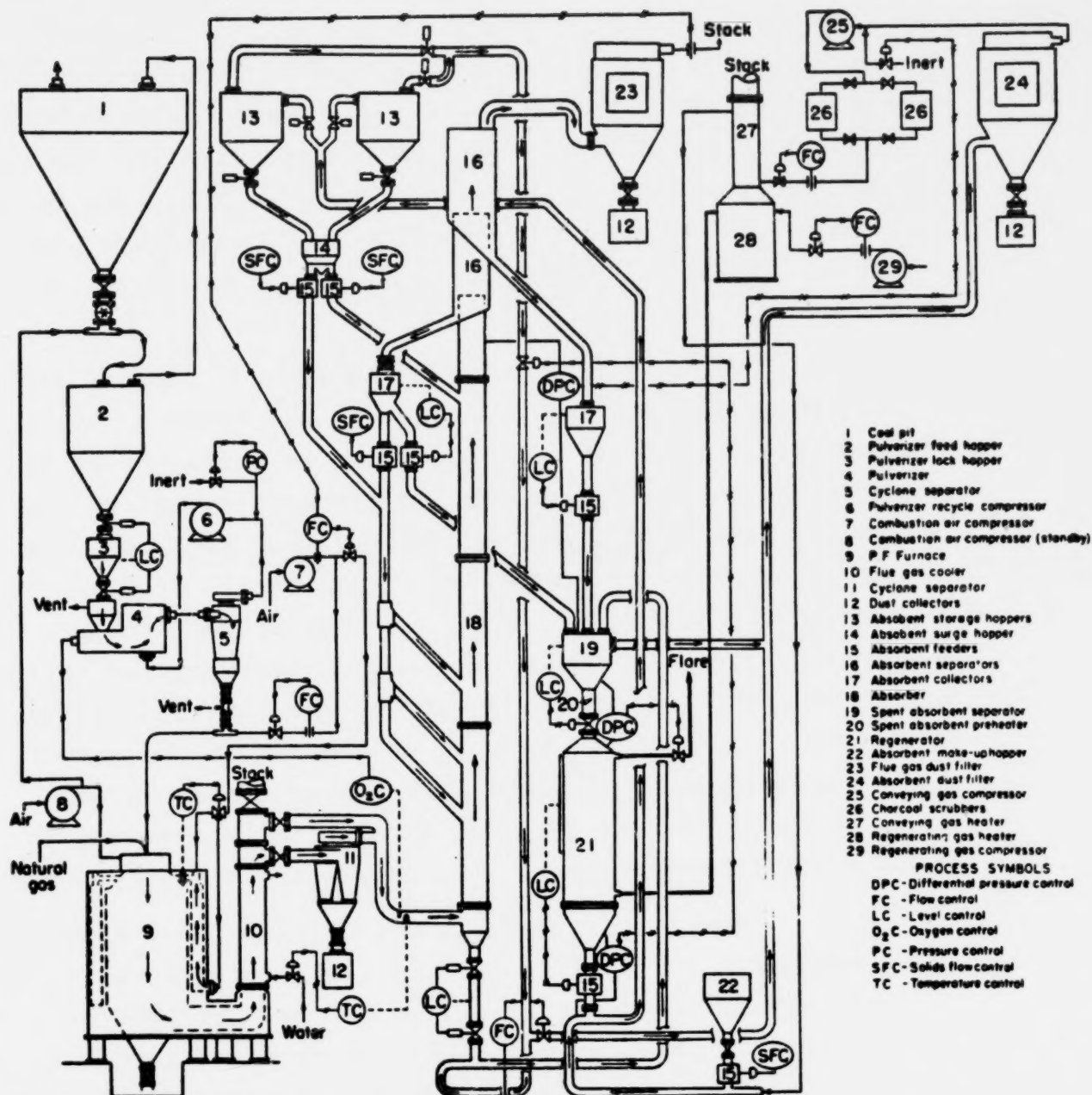


FIGURE 31 -SO₂-Removal pilot plant (55,000 cfh flue gas).

L-9294

From here, the coal is fed, via a lock hopper (3), to the pulverizer (4). A sweep gas entrains the coal in the pulverizer and conveys it to a cyclone (5) where the coal and gas are separated. The coal is then pneumatically conveyed by combustion air from the compressor (7), to the furnace (9). The sweep gas exiting the cyclone is recycled to the pulverizer via compressor (6). The combustion products are cooled to the desired reaction temperature (10) and sent through cyclones (11) for fly-ash removal. The gases enter the sorber (18) where SO_2 is removed by contact with the alkalized alumina sorbent, and exit via a dust filter (23) to the stack.

Sorbent from the sorbent storage hoppers (13) enters the system through the sorbent feed hoppers (14) and feeders (15). The bulk of the sorbent is entrained by the flue gas and passes upward through the sorber (18) to the two solids-disengaging sections (16) (later replaced with a single-stage unit) at the top of the reactor. From the disengaging sections the solids are sent to collection hoppers (17) at which point they are either recycled to the sorber or sent by gravity flow to the regeneration system. The unentrained sorbent falls to the bottom of the sorber and is pneumatically conveyed to the regeneration system. The regenerated sorbent is then pneumatically conveyed to the sorbent storage hoppers (13) completing the solids cycle.

The initial data from the pilot plant described above are given in Table 16 for the test series C, D, E, and F. The data for test series C will not be discussed because the location of the feed points of the feed and particularly the recycle streams were much closer to the bottom of the reactor than for the other tests. As a result the contact time was probably much lower than the subsequent series

TABLE 16 - Operating conditions during absorption tests

Test No.	C101	C201	C401	C501	D101	D102	D103	D104	D105	D106	D107	D108	D109	D110	D111	D112	D113
Gas velocity, ft/sec	25.1	27.1	25.0	25.7	23.4	23.5	23.6	23.6	22.0	22.4	22.6	22.6	22.8	22.8	22.9	22.9	22.8
ΔP , inches H_2O	0.05	0.05	1.00	1.10	0.6	0.7	0.8	0.9	0.8	1.2	1.4	1.6	1.7	0.7	1.0	1.3	1.3
Absorber temperature, °F	631	631	623	598	597	603	608	609	541	546	551	552	558	559	560	559	557
Feed location, ft:																	
Fresh feed	10	10	10	10	20	20	20	20	20	20	20	20	20	20	20	20	20
Recycle	--	--	10	10	20	20	20	20	20	20	20	20	20	20	20	20	20
Feed rates, lb/hr:																	
Fresh feed	114	116	118	123	115	115	115	115	115	115	123	123	123	123	123	123	123
Recycle	0	0	590	674	470	470	470	470	470	470	479	479	479	479	479	479	479
Feed rates, lb/1000 SCF:																	
Fresh feed	4.4	4.4	4.7	5.3	5.0	5.0	5.0	5.0	5.0	4.9	5.2	5.2	5.2	5.2	5.2	5.2	5.2
Recycle	0	0	23.5	29.2	20.3	20.3	20.3	20.3	20.3	20.2	20.3	20.3	20.4	20.4	20.4	20.4	20.4
Recycle to fresh feed ratio, lb/lb	0	0	5.0	5.5	4.1	4.1	4.1	4.1	4.1	4.1	3.9	3.9	3.9	3.9	3.9	3.9	3.9
Bottoms to fresh feed ratio, lb/lb	0.52	0.45	0.60	0.63	0.59	0.58	0.62	0.60	0.79	0.70	0.59	0.56	0.49	0.49	0.50	0.58	0.69
Solid density in absorber, lb/ft ³	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Mean particle size, inch:																	
Fresh feed	0.068	0.066	0.059	0.064	--	--	--	0.052	--	--	--	--	--	--	--	--	--
Bottoms	0.060	--	0.072	0.062	--	--	--	--	--	--	--	--	--	--	--	--	--
Recycle	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Secondary separator, i/	--	--	0.035	0.020	--	--	--	0.039	--	--	--	--	--	--	--	--	--
Bulk solid density, lb/ft ³ :																	
Fresh feed	41.2	--	42.6	44.1	--	--	--	39.4	--	--	--	--	--	--	--	--	--
Bottoms	44.2	--	43.2	47.2	--	--	--	40.8	--	--	--	--	--	--	--	--	--
Recycle	--	--	--	48.5	--	--	--	45.8	--	--	--	--	--	--	--	--	--
Secondary separator, i/	--	--	45.4	46.6	--	--	--	37.9	--	--	--	--	--	--	--	--	--
Sulfur content, wt pct:																	
Fresh feed	0.3	0.3	0.1	0.3	0.5	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4
Bottoms	2.4	--	1.6	1.7	--	--	--	1.3	--	--	--	--	--	--	--	--	--
Recycle	--	--	2.4	3.3	--	--	--	2.2	--	--	--	--	--	--	--	--	--
Secondary separator, i/	--	--	3.0	3.3	--	--	--	2.2	--	--	--	--	--	--	--	--	--
Bench scale activity, g S/100 g	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Sulfur oxides, ppm:																	
10 feet	1830	1740	--	--	--	--	4.07	--	--	--	--	4.64	--	--	--	6.61	--
20 feet	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
30 feet	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
40 feet	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Outlet	1720	1540	460	540	--	--	--	--	--	--	--	--	--	--	--	--	--
Sulfur oxides removal, pct:	--	--	1090	640	370	730	550	840	870	930	1730	1870	1800	1200	1350	1000	1250
Sulfur oxides removal, pct ₂ :	--	--	52.9	64.0	83.9	68.3	76.1	63.7	62.4	59.6	25.5	19.2	22.1	48.1	41.7	56.6	45.9

Continued on next page

Operating conditions during absorption tests
(continued)

Test No.	D114	D115	D119	D120	D121	D122	D123	D124	D125	E101	E102	E103	E104	E105	E106	E107	E108
Gas velocity, ft/sec	22.8	22.7	22.4	21.7	22.2	21.7	21.8	22.2	22.2	26.7	25.5	25.9	26.1	26.2	26.1	26.0	26.1
-P, inches H ₂ O	0.9	1.2	2.8	1.1	1.2	1.2	1.5	1.5	1.5	2.1	1.8	1.5	1.9	1.8	2.2	2.1	2.6
Absorber temperature, °F	556	556	556	513	526	516	548	548	544	604	554	576	599	569	580	574	566
Feed location, ft:																	
Fresh feed	20	20	20	20	20	20	20	20	20	40	40	40	40	40	40	40	40
Recycle	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Feed rates, lb/hr:																	
Fresh feed	123	123	130	177	185	179	179	173	186	186	183	187	190	191	186	186	186
Recycle	479	479	488	488	456	460	432	486	459	1615	1572	1639	1539	1169	1361	1476	1476
Feed rates, lb/1000 SCF:																	
Fresh feed	5.3	5.3	5.6	7.6	7.8	7.7	7.9	7.5	8.0	7.0	6.9	7.1	7.3	7.1	7.0	7.0	6.9
Recycle	20.4	20.5	21.1	20.9	19.3	19.8	19.9	21.1	20.7	60.5	59.1	61.8	59.0	43.5	51.2	55.5	54.9
Ratio to fresh feed ratio, lb/lb	3.9	3.9	3.8	2.8	2.5	2.6	2.5	2.8	2.5	8.7	8.6	8.8	8.1	6.1	7.3	7.9	7.9
Bottoms to fresh feed ratio, lb/lb	0.57	0.46	0.32	0.84	0.53	0.60	0.49	0.43	0.79	0.68	0.35	0.28	0.45	0.54	0.54	0.46	0.54
Solid density in absorber, lb/ft ³	--	--	--	--	--	--	--	--	--	0.17	--	0.15	--	--	--	0.17	--
Mean particle size, inch:																	
Fresh feed	--	0.059	0.056	0.063	0.058	0.064	0.053	0.052	0.050	0.070	0.069	0.068	0.068	0.069	0.065	0.066	--
Bottoms	--	0.058	--	0.057	0.059	0.058	0.058	0.060	0.053	0.066	0.055	0.054	0.052	0.066	0.056	0.055	--
Recycle	--	0.038	0.034	0.035	0.029	0.029	0.033	0.029	0.039	0.025	0.022	0.021	0.018	0.021	0.023	0.024	--
Secondary separator:																	
Solid density, lb/ft ³	--	0.032	0.033	0.023	0.023	0.025	0.025	0.024	0.025								
Fresh feed	--	42.1	44.3	42.2	44.2	42.8	43.6	42.2	43.3	48.7	47.9	48.8	49.7	50.1	48.5	48.6	--
Bottoms	--	43.7	--	43.1	45.6	43.3	44.8	44.3	46.2	47.9	48.5	46.9	49.0	44.0	46.4	45.5	--
Recycle	--	46.7	47.5	47.6	44.5	44.8	44.2	47.4	44.7	50.4	49.9	52.0	48.0	48.9	43.1	46.8	--
Secondary separator:																	
Solid density, lb/ft ³	--	46.9	46.7	43.0	45.6	44.4	47.4	44.7	48.2								
Sulfur content, wt pct:																	
Fresh feed	0.4	0.5	0.6	0.4	0.4	0.4	0.3	0.6	0.6	0.9	0.9	0.8	0.9	0.9	0.8	0.9	--
Bottoms	--	0.9	--	1.0	0.8	1.8	1.0	0.9	--	1.8	2.0	2.0	2.1	1.6	1.4	1.7	--
Recycle	--	3.5	3.2	2.3	2.3	2.2	2.5	1.8	1.1	3.5	3.8	4.4	4.2	4.4	4.0	--	--
Secondary separator:																	
Solid density, lb/ft ³	--	2.7	3.1	2.3	2.3	2.7	2.5	3.0	2.5	--	--	--	--	--	--	--	--
Bench scale activity, g S/100 g	--	--	--	5.23	--	--	--	4.10	--	--	9.6	--	--	--	9.6	--	--
Sulfur oxides, ppm:																	
20 feet	--	--	1830	1750	1880	2110	1870	1440	1890	1690	1900	1810	1640	1820	1740	1910	2120
20 feet	--	--	1950	1250	1590	1750	1750	2200	1810	1590	1480	1460	1300	1710	1330	1360	1550
20 feet	--	--	1150	1290	1540	1600	1330	1340	1560	1150	1200	1200	1030	1800	1190	900	1740
20 feet	--	--	1100	1210	1080	1230	1270	1050	1070	220	1080	1220	990	1010	580	690	1130
Outlet	1220	1210	810	830	590	710	550	440	670	100	520	560	400	550	320	260	430
Sulfur oxides removal, pct ₂	47.3	47.6	65.0	64.1	74.6	69.3	76.2	80.8	71.0	95.8	77.7	75.8	82.5	76.4	86.1	88.8	81.2

Continued on next page

Operating conditions during absorption tests
(continued)

Test No.	E109	E110	E111	E112	E113	E114	F101	F102	F103	F104	F105	F106	F107	F108	F110	F112
Gas velocity, ft/sec	25.0	25.0	24.9	25.0	25.4	25.3	26.8	26.8	28.2	29.0	27.9	28.1	26.6	27.7	29.4	26.6
ΔP, inches H ₂ O	--	--	--	--	--	--	0.3	0.1	1.6	1.6	1.9	1.6	1.5	0.6	0.3	1.5
Absorber temperature, °F	567	567	558	562	577	591	602	583	584	596	565	548	513	544	588	496
Feed location, ft:																
Fresh feed	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40
Recycle	20	20	20	20	20	20	--	--	20	20	20	20	20	20	--	20
Feed rates, lb/hr:																
Fresh feed	187	187	187	187	187	187	187	187	187	187	187	187	187	187	187	187
Recycle	1552	1552	1552	1552	1552	1552	0	0	1851	1830	1851	1871	1851	1851	0	1551
Feed rates, lb/1000 SCF:																
Fresh feed	7.2	7.2	7.2	7.2	7.2	7.3	7.1	7.0	6.7	6.5	7.0	6.5	6.6	6.5	6.5	6.5
Recycle	60.2	60.0	59.7	59.9	59.8	60.3	0	0	65.9	63.9	69.1	64.6	64.9	64.5	0	53.5
Recycle to fresh feed ratio, lb/lb	8.3	8.3	8.3	8.3	8.3	8.3	0	0	9.9	9.8	9.9	10.0	9.9	9.9	0	8.3
Bottoms to fresh feed ratio, lb/lb	0.71	0.64	0.73	0.65	0.61	0.50	0.60	0.53	0.84	0.75	0.55	0.78	0.69	0.54	0.63	0.72
Solid density in absorber, lb/ft ³	--	--	--	--	--	0.16	0.03	--	0.13	0.15	0.13	0.15	0.16	0.09	0.03	0.13
Mean particle size, inch:																
Fresh feed	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Bottoms	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Recycle	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Secondary separator ^{1/}	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Bulk solid density, lb/ft ³ :																
Fresh feed	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Bottoms	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Recycle	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Secondary separator ^{1/}	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Sulfur content, wt pct:																
Fresh feed	1.3	1.3	1.4	1.2	1.3	1.4	0.5	0.6	0.5	0.5	1.8	1.8	1.9	1.8	--	2.2
Bottoms	1.9	2.0	1.5	1.4	1.6	1.8	1.1	1.1	1.6	1.7	3.4	3.4	3.3	3.6	--	2.8
Recycle	4.3	4.8	5.4	5.4	4.7	3.9	--	--	4.7	5.6	4.3	5.8	6.1	4.6	--	6.7
Secondary separator ^{1/}	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Bench scale activity, g S/100 g	--	--	9.8	--	--	--	--	--	--	--	--	--	--	--	--	--
Sulfur oxides, ppm:																
10 feet	1910	1910	1970	2140	920	2170	2330	2310	2100	2060	1920	1330	1620	1850	2130	2080
20 feet	1430	1440	1340	2420	2030	1930	2430	2270	1710	2250	1910	830	1560	2030	2400	1760
30 feet	990	1190	1230	--	1620	--	2240	2170	1590	1400	1390	1200	1116	1580	2160	1210
40 feet	420	960	1030	1760	--	1660	2040	2080	1300	820	1340	1180	1050	1170	2170	1480
Outlet	240	1180	410	1100	810	750	--	1920	160	280	780	700	200	540	2020	730
Sulfur oxides removal, pct ^{2/}	89.6	49.0	82.1	52.5	65.1	67.5	--	17.2	93.3	88.1	66.1	69.7	91.4	76.8	12.7	68.4

1/ Secondary separator not used during test series E and F

2/ Percent removal based on average inlet sulfur oxides concentration of 2314 ppm.

of tests. Runs 1 through 19 of the D series were conducted using a recycle ratio of approximately 4:1 whereas runs 20 through 25 had a recycle ratio of approximately 2.5:1. The average SO₂ removal for the entire D series was 58%, with the runs at the 4:1 recycle ratio averaging 52% and the runs at the 2.5:1 recycle ratio giving an average of 75% removal. The higher removal for the lower recycle ratio was not unexpected, however, because of the following reasons: Although the recycle ratio was changed in the latter D series runs the amount of recycle remained the same as in the earlier runs while the amount of fresh feed was increased; therefore, the total amount of sorbent cycling in the sorber increased as did the percentage of fresh feed. The greater sulfur removal in the latter D series runs reflects this and indicated, as expected, that the SO₂ removal is a function of the solids density in the sorber. This conclusion is further supported by the E and F series runs with recycle, during which average sulfur removals of 76 and 79%, respectively, were obtained.

In the E and F series, 4 runs, E-101, E-109, F-103, and F-107 apparently removed 90% of the inlet SO₂. However, in two of these runs, E-101 and F-107, approximately 30% of the SO₂ was removed in the first 10 feet of the sorber. Furthermore, the results of run E-109 could not be duplicated in run E-110 even though apparently identical operating conditions were used. It was also noticed that in 6 of the 24 E and F series runs, SO₂ concentration increased between the sample points in the reactor. The reasons for this are not apparent but could be caused by stripping of SO₂ from the sorbent or possible inaccuracies in the gas sampling mechanism or SO₂ analyses. Therefore, owing to the variation in SO₂ removal obtained in some cases for what are apparently essentially identical operating conditions, and because only a few runs

actually achieved 90% removal, it is felt that 90% removal has not been adequately demonstrated.

Since in most of the test runs made in the 55,000 CFH pilot plant more than one variable was changed (e.g., gas velocity, pressure drop, solids to gas ratio, etc.), the results of several tests using similar operating conditions were combined and averaged. Figure 32 shows the average SO_2 removal obtained under similar operating conditions as a function of column height. For these runs, average sulfur removals of 80% were obtained and a distinct relationship between SO_2 concentration and a column height can be seen. On the whole, test series E and F runs with high recycle demonstrated average sulfur removals of 70 to 80% and it is believed that when an acceptable sorbent is developed, 90% removal can be obtained in the dispersed phase type reactor.

In order to test the sorption model at higher sorbent densities and sulfur loadings, a number of high recycle ratio runs, series H, were made. The data for these runs are tabulated in Table 17. Although recycle ratios of 15:1 were attempted and the average recycle ratio was nearly 11:1 during 12 of the runs, no improvement in sulfur removal was obtained. For the 12 series H runs at recycle ratios of 7:1 or greater the average removal was 60.2%.

Even though the removal levels are lower in the H series than in the E or F series, definite conclusions as to the effect of high recycle operation cannot be made, for the sorbent activity had decreased from 9.8 to 6.2 grams of sulfur per 100 grams of sorbent and the sorbent sulfur levels at which the runs were made were much higher than had previously been used. The USBM-Albany in their testing program had shown that sorption rate is a function of the sulfur loading on

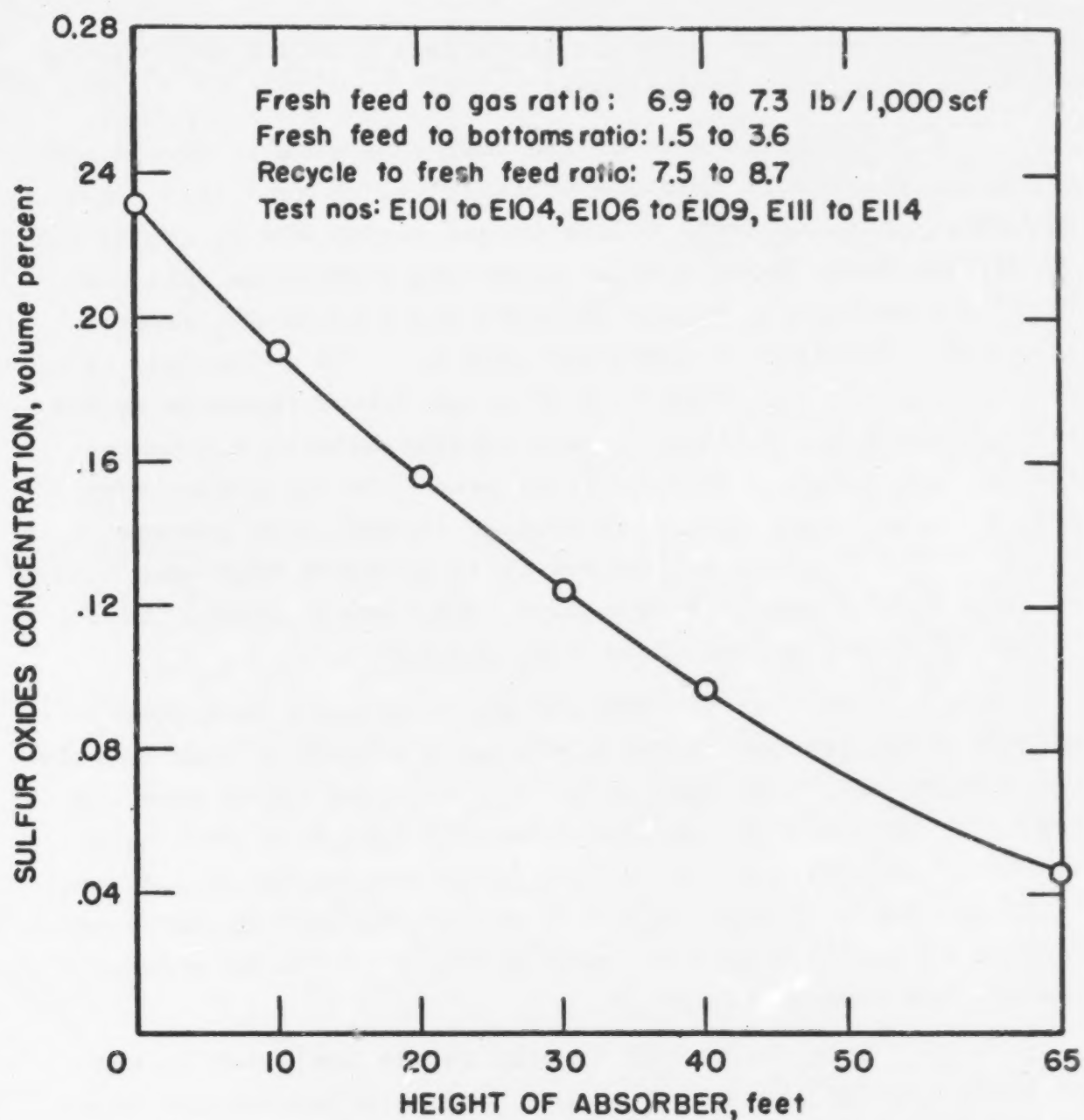


FIGURE 32—Average sulfur oxides concentration as function of absorber height when total overheads are recycled at 20 foot level and fresh feed introduced at 40 foot level.

TABLE 17 - Operating conditions during sorption tests

Test No.	M101	M102	M103	M104	M105	M106	M107	M108	M109	M110	M111	M112	M113	M114	M115	M116	M117	M118	M119
Gas velocity, ft/sec	25.9	25.2	27.0	26.6	27.5	27.4	26.9	30.0	28.9	28.5	28.3	28.6	28.7	29.2	28.8	30.4	26.6	25.2	26.5
ΔP , inches H ₂ O	0.15	1.53	1.64	1.70	1.1	0.3	0.2	0.36	1.25	1.87	1.87	1.53	1.68	1.56	1.70	0.3	1.88	1.96	1.93
Absorber temperature, °F	608	564	587	565	602	571	578	585	555	552	546	563	562	577	567	610	564	555	548
Feed location, ft:																			
Fresh feed	40	20	20	20	20	40	40	40	40	40	40	40	40	40	40	40	40	40	40
Recycle	197	197	197	197	197	207	111	206	194	194	199	181	2227	137	212	212	208	209	219
Feed rates, lb/hr:																			
Fresh feed	0	1605	1532	2302	812	0	0	0	803	1602	2299	2107	181	2227	2181	2123	0	2195	2285
Recycle	7.6	7.6	7.2	7.2	7.2	7.5	3.8	6.8	6.5	6.5	6.7	6.1	6.1	4.6	7.1	7.1	7.6	8.0	7.9
Feed rates, lb/1,000 SCF:																			
Fresh feed	0	62.0	56.3	86.2	29.8	0	0	0	26.8	56.0	77.5	71.2	75.1	73.5	71.5	0	79.9	87.5	86.1
Recycle	0	8.1	7.8	11.7	4.1	0	0	0	4.1	8.3	11.6	11.6	12.3	13.9	10.0	0	10.6	10.9	10.9
Recycle to fresh feed ratio, lb/lb																			
Bottoms to fresh feed ratio, lb/lb	0.47	0.59	0.57	0.60	0.48	0.44	0.45	0.30	0.34	0.51	0.41	0.21	0.34	0.32	0.34	0.29	0.36	0.43	0.46
Solid density in sorber, lb/cu ft	0.03	0.14	0.15	0.15	0.10	0.04	0.03	0.03	0.10	0.16	0.17	0.14	0.16	0.15	0.17	0.03	0.14	0.20	0.15
Mean particle size, inch	0.064	0.064	0.066	0.064	0.068	0.070	0.071	0.077	0.073	0.075	0.071	0.073	0.074	0.074	0.070	0.079	0.068	0.072	0.070
Fresh feed	0.034	0.017	0.021	0.019	0.026	0.024	0.017	0.020	0.036	0.027	0.023	0.023	0.020	0.020	0.018	---	0.015	0.017	0.018
Bottoms	0.034	0.017	0.021	0.019	0.026	0.024	0.017	0.020	0.036	0.027	0.023	0.023	0.020	0.020	0.018	---	0.015	0.017	0.018
Recycle	0.059	0.035	0.045	0.031	0.055	0.063	0.063	0.074	0.058	0.053	0.042	0.040	0.049	0.047	0.032	0.072	0.074	0.020	0.023
In sorber	49.4	49.4	46.7	46.7	45.1	51.9	51.4	51.5	48.6	48.6	49.9	45.4	45.4	45.4	45.4	2.21	52.2	52.4	54.9
Bulk solid density, lb/cu ft:																			
Fresh feed	47.2	44.7	46.7	46.0	45.1	44.9	44.3	43.4	45.7	44.4	47.4	45.9	44.9	44.9	44.2	1.74	47.9	48.8	51.0
Bottoms	49.9	50.1	47.8	52.3	50.7	51.9	51.4	51.7	50.1	50.0	52.2	47.9	50.6	49.6	48.2	---	49.9	51.9	54.0
Recycle	45.4	51.0	47.8	51.7	47.2	48.3	49.6	48.9	50.5	48.6	53.2	52.3	51.9	50.9	51.4	2.43	50.4	48.8	55.6
In sorber	1.31	---	---	---	---	3.99	4.09	4.54	3.13	3.13	3.78	0.59	0.59	0.59	0.59	3.93	2.94	3.74	3.93
Sulfur content, wt %:																			
Fresh feed	1.37	2.18	2.04	2.72	2.38	2.34	2.48	2.28	2.55	2.51	2.79	1.80	1.50	1.72	1.84	3.09	2.69	2.83	3.09
Bottoms	2.38	5.00	4.48	5.77	4.91	5.39	6.16	5.68	4.54	5.18	5.78	3.16	3.00	3.02	3.61	6.57	6.60	5.24	6.67
Recycle	1.62	4.34	3.72	5.33	3.58	3.02	2.96	2.63	3.72	4.36	5.39	3.78	2.60	2.98	3.79	6.40	4.61	6.11	6.40
In sorber	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Bench scale activity, S/100 S	1790	1960	1625	1873	1760	1670	1590	1340	1430	1640	1650	1470	1380	1506	1630	1510	1670	1990	1480
Sulfur oxides, ppm:																			
Inlet	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
10 feet	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
20 feet	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
30 feet	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
40 feet	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Outlet	1470	750	665	609	1100	1420	1560	1060	880	870	650	570	530	480	550	1410	680	850	780
Sulfur oxides removal, pct	18.1	61.8	59.1	67.5	27.3	14.9	1.5	30.1	38.6	47.1	60.7	61.1	66.3	68.4	66.6	6.6	59.5	57.2	47.1
Sorbent collected on fabric filter, pct of fresh feed	---	1.79	2.79	2.60	0.92	0.54	---	1.71	1.19	1.99	3.96	5.51	5.62	7.74	3.07	1.59	5.23	4.68	2.05

the sorbent (see Figure 16) and that as the sulfur loading approaches the saturation level the sorption rate decreases drastically. It should be noted also that in most of the runs (11 out of 15 for which the data are reported) the sulfur content of the bottoms stream is less than the fresh feed. Further, since the bottom stream comprises from about 20 to 60% of the fresh feed rate, it appears that a substantial portion of the fresh feed is not removing any SO_2 and thus the effective fresh feed rate is much smaller than the actual rate. Therefore, it is improbable that high percentage removals of SO_2 could be obtained at these conditions of low gas residence times, high sorbent sulfur loadings, and by-passing of a significant amount of the fresh feed, at which the H series tests were operated. The fact that even 60% removal levels were obtained under these conditions is, in itself, promising.

Further tests, series K and series M runs, were made to evaluate properties of two new sorbents, Grace-2 and Kaiser-1, respectively. Data from these tests are listed in Table 18. Many of the previously reported operating parameters were not presented in these data, thus precluding direct comparisons with earlier tests. The average removal for the Grace-2 sorbent during the K series test was 51%. The average removal in the M series tests which used the Kaiser sorbent was 47%; however, the last two runs of this series, M-105 and M-106, gave sulfur removal levels of 89 and 83%, respectively.

Because of the relatively small sulfur pickup by the bottoms fraction, it has been suggested that a bottoms recycle system be added to the present pilot plant. This type of system would increase the solids residence time of

TABLE 18- Sorption operating conditions for evaluation of Grace No. 2 and Kaiser No. 1 sorbents

Test No.	K100 Grace No. 2	K101 Grace No. 2	K102a Grace No. 2	K102b Grace No. 2	K103a Grace No. 2	K103b Grace No. 2	K104 Grace No. 2	K105a Grace No. 2	K105b Grace No. 2
Sorbent used	1	1	1	1	2	2	3	3	3
Sorption-regeneration cycle	1	1	1	1	2	2	3	3	3
Sulfur oxides concentration, mole fraction:									
Inlet, (y_0)	0.00145	0.00188	0.00172	0.00156	0.00183	0.00153	0.00166	0.00157	0.00218
Exit, (y_f)	0.00067	0.00082	0.00081	0.00057	0.00110	0.00075	0.00107	0.00085	0.00095
Flue gas flow rate, SCFH, (V)	24,700	24,600	24,500	24,300	24,500	24,100	24,500	24,700	22,700
Sorber pressure loss, inches H ₂ O (p)	1.23	1.22	1.25	1.25	0.89	0.89	0.62	0.81	0.96
Sulfur content of sorbent feed, wt fract.S, (x_0)	0.0056	0.0033	0.0054	0.0048	0.0084	0.0084	0.0138	0.0105	0.0054
Sorbent feed rate, lb/hr, (L_f)	175	178	179	184	170	182	218	187	183
Sorber temperature, °F	528	540	548	554	543	559	551	553	576
Solid density in sorber, lb/cu ft	0.098	---	0.090	---	0.065	0.076	0.045	0.072	0.099
Sorbent carried from reactor, pct of feed	---	---	---	---	←-----0.52-----→	←-----0.52-----→	←-----0.70-----→	←-----0.70-----→	←-----0.70-----→
Sorbent <60 Tyler mesh carried from reactor, pct of feed	---	---	---	---	←-----0.40-----→	←-----0.40-----→	←-----0.55-----→	←-----0.55-----→	←-----0.55-----→
Sorption rate, wt SO ₂ removed/wt sorbent/hr, (r) 1/2	0.89	1.22	1.01	1.10	1.14	1.20	1.33	1.25	1.65
Sorption rate constant (K) 2/	8.98	8.93	8.85	11.33	10.17	13.89	16.31	15.29	13.02

Continued on following page

TABLE 18- Sorption operating conditions for evaluation of Grace No. 2 and Kaiser No. 1 sorbents, con.

Test No.	M100a	M100b	M101	M102	M103a	M103b	M105	M106
Sorbent used	Kaiser No. 1	Kaiser No. 1	Kaiser No. 1	Kaiser No. 1	Kaiser No. 1	Kaiser No. 1	Kaiser No. 1	Kaiser No. 1
Sorption-regeneration cycle	1	1	2	3	4	4	5	6
Sulfur oxides concentration, mole fraction:								
Inlet, (y _o)	0.00164	0.00134	0.00190	0.00184	0.00209	0.00157	0.00168	0.00144
Exit, (y _f)	0.00099	0.00089	0.00127	0.00127	0.00133	0.00107	0.00019	0.00024
Flue gas flow rate, SCFH, (V)	25,200	27,000	27,800	27,200	27,200	27,100	29,400	28,900
Sorber pressure loss, inches H ₂ O (p)	0.82	0.88	0.68	0.74	0.66	0.71	3.11	1.93
Sulfur content of sorbent feed, wt fract.S, (x _o)	0.0026	0.0015	0.0046	0.0049	0.0046	0.0057	0.0132	0.0135
Sorbent feed rate, lb/hr, (L _f)	200	198	204	201	226	206	230	1326
Sorber temperature, °F	577	599	539	561	558	556	526	559
Solid density in sorber, lb/cu ft	0.069	0.088	0.089	0.068	0.064	0.064	---	0.178
Sorbent carried from reactor, pct of feed	←-----0.60-----→	←-----0.60-----→	0.96	---	←-----1.10-----→	←-----1.10-----→	9.02	0.65
Sorbent <60 Tyler mesh carried from reactor, pct of feed	←-----0.53-----→	←-----0.53-----→	0.84	---	←-----0.93-----→	←-----0.93-----→	6.20	0.58
Sorption rate, wt SO ₂ removed/wt sorbent/hr, (r) ₁	1.14	0.78	1.46	1.19	1.78	1.07	0.80	1.02
Sorption rate constant, (K) ₂	5.40	2.41	7.74	6.35	8.98	7.00	21.90	20.46

1/ Sorption rate defined as

$$r = \frac{0.0342(y_o - y_f)V}{0.601 p}$$

2/ Sorption rate constant defined as

$$K = \frac{r(x_o - x_f)}{2[y_o]^{2/3} \frac{1}{9} C_h y_o^{2/3} \frac{1}{108} C_h^{1/3}} \quad \text{where}$$

$$x_f = \frac{x_o L_f + 0.089(y_o - y_f)V}{L_f + 0.225(y_o - y_f)V}$$

$$C_h = 3[y_o^{1/3} - y_f^{1/3}]$$

the larger less loaded sorbent pellets. Kinetic studies have shown that these low sulfur content particles should be more reactive than the smaller highly loaded particles which have been recycled in the earlier tests. Based on the above, the Bruceton pilot plant was altered so that the effect of a bottoms recycle could be evaluated. The new design is shown in Figure 33. At this time, however, no data using alkalized alumina sorbent have been received and the effect of bottoms recycle on SO_2 removal cannot be evaluated.

(4) AVCO

The role of the AVCO Corporation in the study of alkalized alumina sorption was directed toward kinetic modeling. Their sorption model, which will be discussed in a later section of this report, is based on sorption data such as that shown in Table 19. Additional AVCO data are available in their reports and are not included here. A plot of these typical data (in the form of a rate expression vs. sorbent loading) is presented in Figure 34 and a comparison of these data to those predicted by calculations based on mass transfer to single spheres is shown in Table 20. The variables used in Figure 34 are as follows:

- y = mol fraction of SO_2 in the vapor
- W = sorbent loading, lbs. of SO_2 gained/lb sorbent.
- W_C = sorbent loading @ saturation, lbs. of SO_2 gained/lb sorbent.

With the exception of the initial loading region 0 - 0.02 lb SO_2 /lb sorbent, the sorption rates were accurately described by the model.

TABLE 19

SORBENT LOADING TEST DATA

ISR-3

ISR-4

ISR-5

-----Weight of sorbent = 217 mg-----

Time	Weight gain (mg)	Time	Weight gain (mg)	Time	Weight gain (mg)
0 sec	0	0 sec	0	0 sec	0
8.3	1.4	5	.5	5	1
15.0	1.7	10	.8	10	1.2
22.5	2.1	15	1.0	15	1.5
30.0	2.4	20	1.6	30	1.9
45.0	2.7	25	1.9	45	2.2
1 min	3.2	30	2.0	1 min	2.8
1.5	3.8	40	2.0	1.5	3.1
2	4.0	50	2.5	2	3.7
3	5.1	60	3.1	3	4.4
4	6.3	1.25 min	4.4	5	5.3
5	6.4	1.50	4.7	10	7.0
7	8.0	1.75	4.7	15	8.7
10	9.0	2.0	5.0	20	9.7
15	10.8	2.5	5.7	25	11.0
20	12.4	3.0	6.0	35	13.5
25	13.9	5.25	7.4	45	15.8
30	15.1	8	8.0	55	17.9
35	16.1	10	9.7	65	19.2
40	17.2	15	12.0	75	22.0
45	18.3	20	12.9	79	23.0
50	19.2	25	14.5		
60	21.0	35	17.2		
80	25.7	45	19.0		
85	26.6	55	21.0		
		65	22.7		
		75	24.3		
		85	25.4		

-----Weight of sorbent = 356 mg-----

ISR-2¹ISR-4¹ISR-5¹

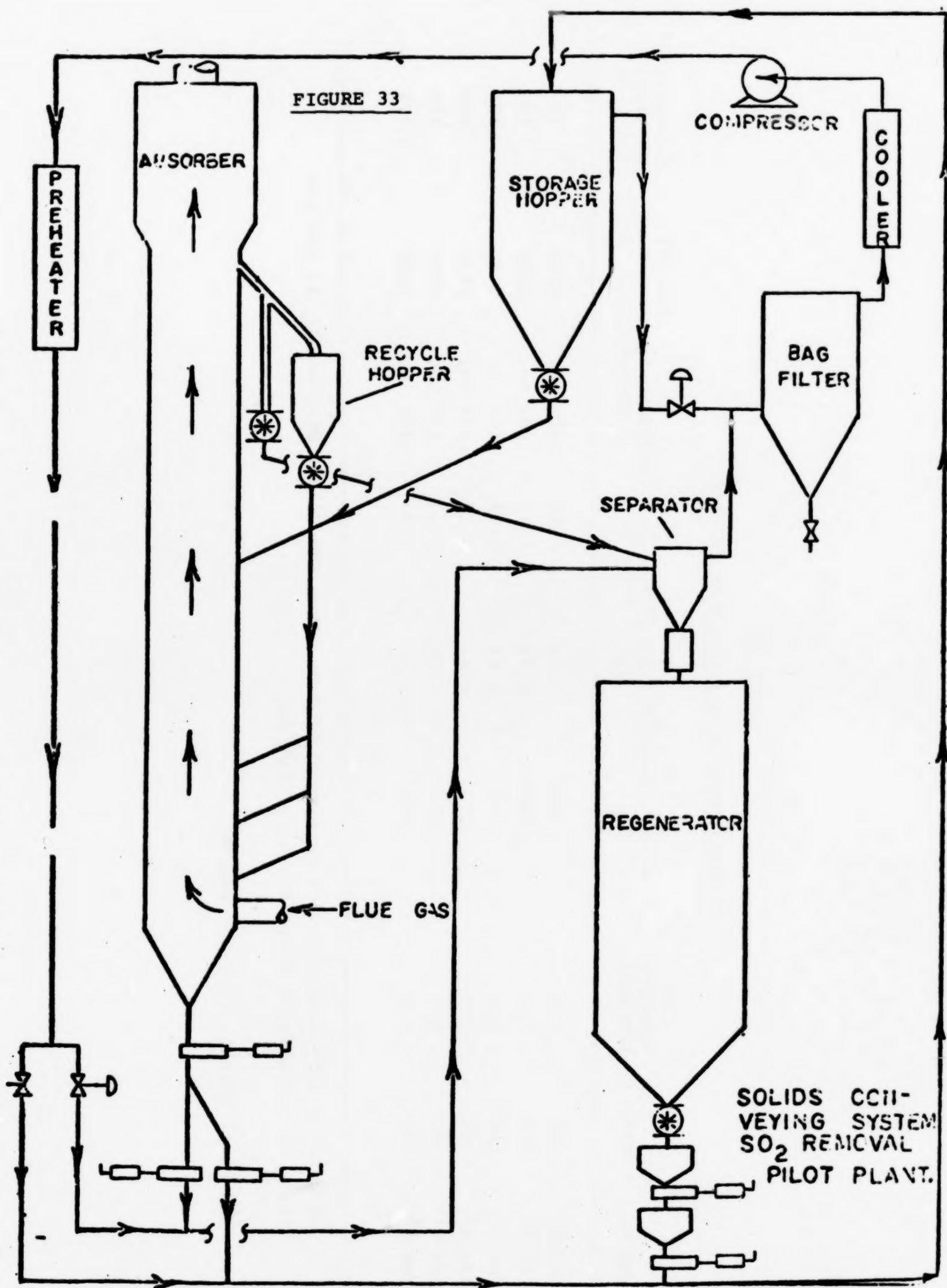
Time	Weight gain (mg)	Time	Weight gain (mg)	Time	Weight gain (mg)
0 sec	0	0 sec	0	0 sec	0
5	2.3	5	2.3	5	2.9
10	2.8	10	3.7	10	4.9
15	3.6	15	4.3	15	6.7
20	3.7	20	4.6	20	7.9
25	4.0	25	4.9	25	8.7
30	4.2	30	5.1	30	9.2
45	4.3	45	5.7	45	9.8
1 min	4.7	1 min	5.9	1 min	9.9
1.5	5.2	1.5	6.4	1.5	10.7
2	5.6	2	7.0	2	11.3
3	6.4	3	7.8	3	12.1
4	7.0	4	8.9	4	13.0
5	7.9	5	9.6	5	13.7
10	10.5	10	12.6	10	16.7
15	12.8	15	15.6	15	19.8
25	16.6	25	20.6	20	21.7
35	20.6	35	25.7	30	25.8
50	25.4	50	32.0	40	29.8
65	30.2	65	38.2	60	37.1
75	33.7	80	44.7	80	44.6
80	35.0	90	48.7		

TABLE 20
SUMMARY DATA OF INITIAL RATE STUDIES¹⁾

Run No.	T (°C)	Gas Velocity (ft/sec)	SO ₂	Vol. Percent H ₂ O	O ₂	Particle Diameter	Initial Rate From Data, hr ⁻¹	Calculated* Initial Rate, hr ⁻¹
ISR-3	300	1.9	.0695	6.42	3.12	.102 in.	4460	990
ISR-4	300	1.9	.0695	6.42	3.12	.102 in.	2260	990
ISR-5	300	1.9	.0695	6.42	3.12	.102 in.	5260	990
ISR-2 ¹⁾	300	1.9	.0599	4.32	3.19	.102 in.	8632	990
ISR-4 ¹⁾	300	1.9	.0585	6.42	3.12	.102 in.	2760	990
ISR-5 ¹⁾	300	1.9	.0562	10.4	2.99	.102 in.	9260	990

* Computed as mass transfer rate to single spheres using the volume percent SO₂ in the gas stream as the driving force for mass transfer.

1) AVCO Final Report, 11-1-67, pg. 94.



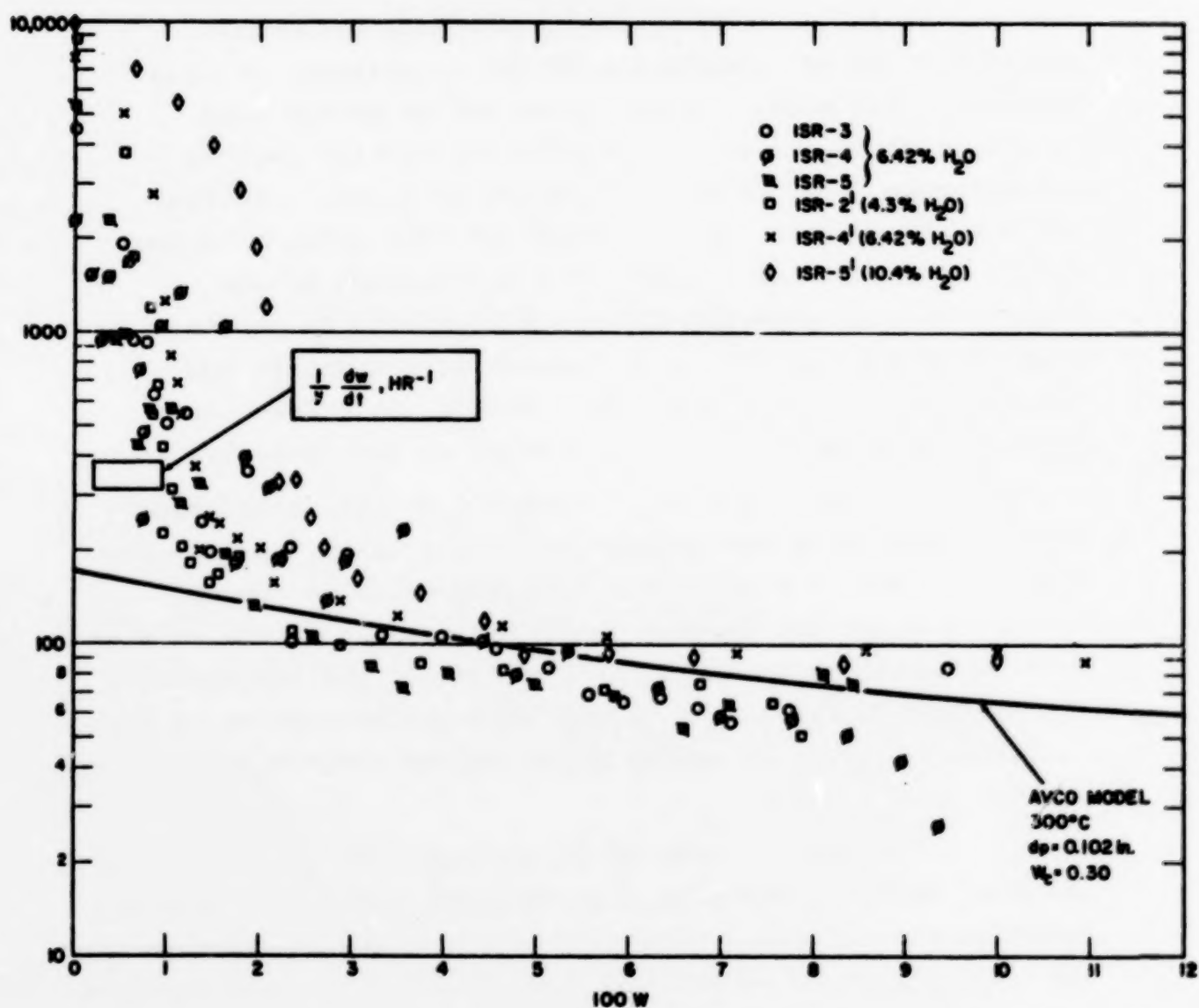


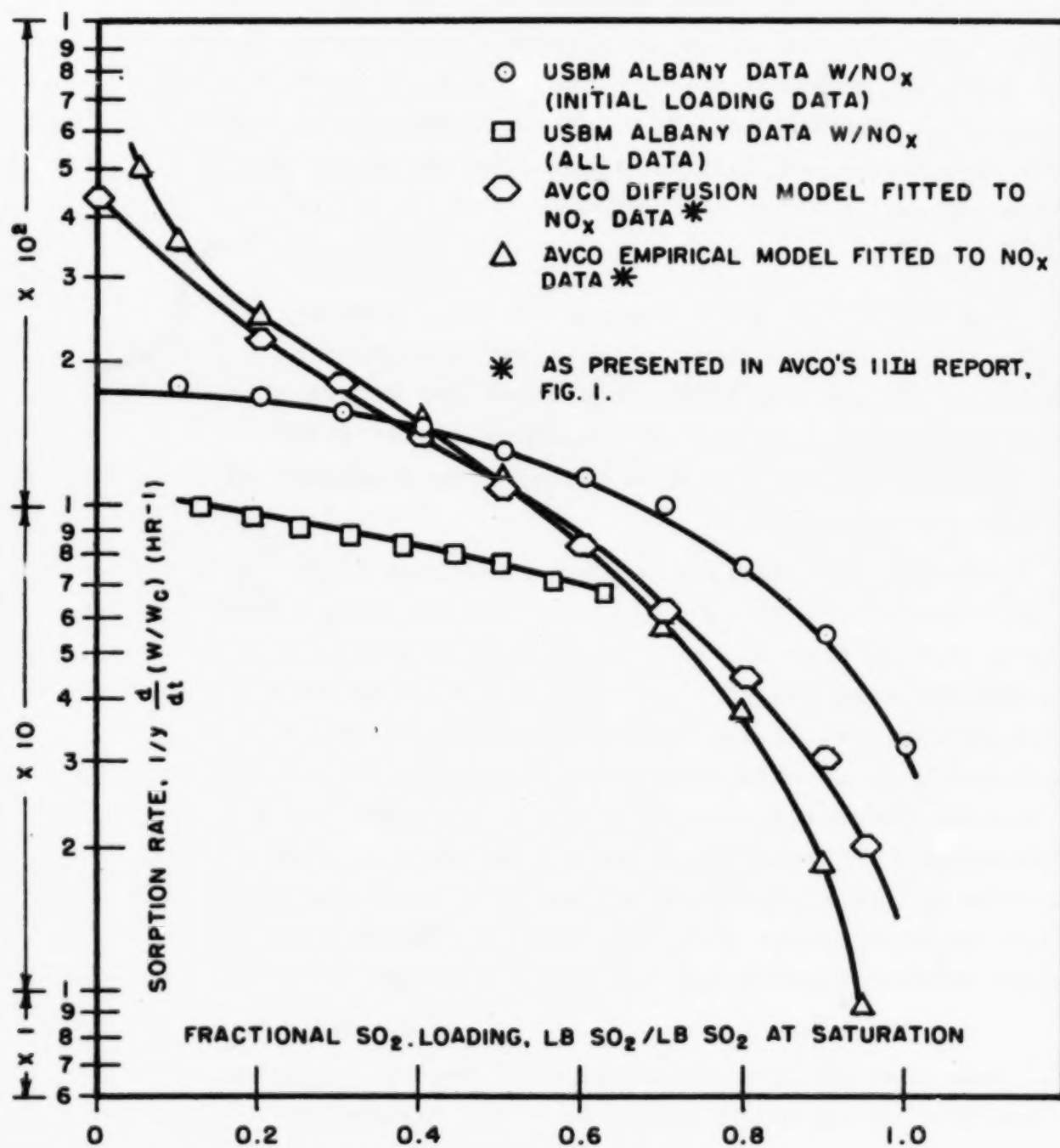
FIGURE 34 INITIAL SORPTION RATE DATA

These rates were then compared to USBM-Albany, (NO_x)-free sorption data. The initial USBM rates were considerably lower than the initial rates measured at AVCO. This may be due to differences in sorption properties, particle diameter, resolution of the experiment, or mass transfer limitations. Also, there was evidently some depletion of SO₂ in the gas during the initial part of the sorption. The USBM-Albany rates at higher loadings are also lower than those measured at AVCO but not to the extent of the initial rates. The differences at the higher loadings probably reflect differences in sorbent properties and particle size because mass transfer and the resolution of the experiment should not present the problems that they might have created at the lower loadings.

One factor which appeared to influence these high initial rates was water vapor. Initially, as seen in Figure 34, the rate increases with the moisture content of the flue gas but appears to be independent of the moisture level at loadings greater than 2 percent. The independence of moisture content is in accord with the assumption of pore diffusion control, an effect which is realized at loadings greater than 2 percent.

When the role of NO_x on sorption became apparent, the AVCO model's constants were adjusted and a new empirical equation was defined. Although the new equation, representing the AVCO NO_x data, showed the same deviation at both the lower and higher range of sorbent loadings when compared with the USBM-Albany's NO_x data (Figure 35), the mid-range sorption rates compared favorably. Since it is in this middle range that commercial sorbers will operate, the corroboration of the Albany data by AVCO is deemed sufficient from a design point of view.

FIGURE 35
COMPARISON OF USBM ALBANY AND AVCO SORPTION RATES OF SO₂
ON
ALKALIZED ALUMINA WITH NO_x PRESENT



(5) W. R. Grace

W. R. Grace and Company is one of the major sorption manufacturers; as such, their work has been directed toward improved sorbent manufacture, mechanical properties, binder and additive effects. In evaluating the effectiveness of these improvements, however, they have necessarily been involved in sorption studies. These bench-scale studies, in general, agree quite well with the sorption work of the USBM-Albany and the AVCO Corporation. For the most part, these studies were based on NO_x -free flue gases and further discussion of these data is not warranted in light of the improved sorption effects found in the NO_x data.

Although the Grace results for NO_x sorption indicate sorption rate increases of the same magnitude as were reported by Albany and AVCO, they found one effect which had not been reported by either of the other two sorption analysts. This effect was the high surface concentration of sodium sulfate, Na_2SO_4 .

It was hypothesized by Grace that the high level of SO_3 dictated by the NO_x chemistry would cause rapid conversion of the surface sodium aluminate to Na_2SO_4 . This theory is supported by the data shown in Table 21 in which the results of analyses of the sulfate content of the "fines" and "cores" produced by attrition are tabulated. On the average, sulfate concentration of the fines (assumed to be surface fragments) is higher by a factor of 3.6 than that which is found in the sorbent cores. For comparison an NO_x -free run is presented. This run shows a fairly even distribution between surface and interior loadings.

The increased reactivity in the presence of NO_x was visualized, therefore, as the result of Na_2SO_4 crystals crowding one another as sorption occurs. The crystalite

TABLE 21

SO₄ Determination of Sorbent Exposed to

Flue Gas Containing NO_x After Attrition¹⁾

<u>SAMPLE NO.</u>	<u>"Cores" Wt. % SO₄*</u>	<u>"Fines" Wt. % SO₄*</u>
5526-28	8.43	37.3
5526-30	7.24	23.7
5526-32	5.96	24.6
5526-33	13.14	11.05**
5526-34	7.12	17.83

* All samples contain from 2 to 3 wt. % SO₄ before sorption.

** No NO_x in feed gas.

1) W. R. Grace, Monthly Report, Aug. 1968, Pg. 2.

growth of Na_2SO_4 at the sorbent surface causes fractures and cracks to develop. The increased surface area created by these cracks exposes more fresh sorbent thus increasing sorption rate. The increased sorbent attrition rates associated with the NO_x sorption studies further support this hypothesis.

To remedy this situation, Grace is studying the possibility of impregnating the Dawsonite material on a suitable support. Ideally, this support would increase the mechanical properties of the sorbent by limiting the extent to which surface cracking could proceed while not greatly inhibiting the excellent reactivity or regenerability of the present material. In addition, Grace is also evaluating the use of binders to stabilize the sorbent structure as a means of improving attrition resistance.

(6) CEGB (Central Electricity Generating Board)

The work of CEGB has been in the areas of sorbent evaluation and pilot plant development, but not much of the actual data has been reported. However, CEGB have reported their conclusions obtained from these data. A summary of these conclusions for alkalized alumina sorption of SO_2 is given below.

In synthetic flue gas, SO_2 removal takes place as sulfite at low temperatures and sulfate at high temperatures. The temperature range studied is from below 100°C to above 350°C . In actual flue gases, however, SO_2 removal is to the sulfate form regardless of the sorption temperature. This was not fully explained by CEGB but they did indicate that nitrogen oxides appeared to exert a strong catalytic effect on sorption, particularly in the surface density of the sorbent. This last conclusion agrees quite well with the W. R. Grace results discussed earlier and the effects

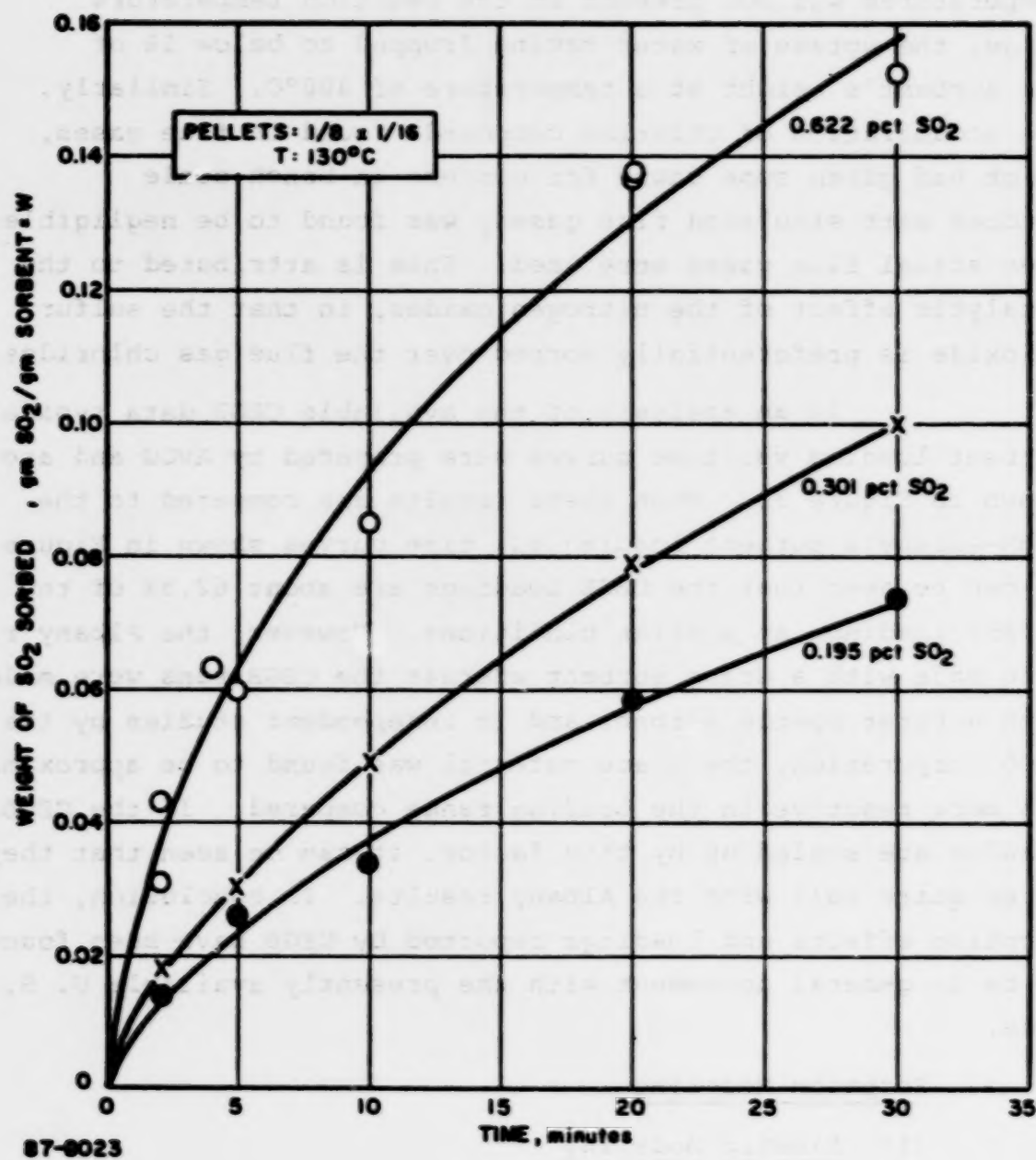


FIGURE 36 -SO₂ SORPTION CURVES OF CERL

of temperature on sorption in both synthetic and actual flue gases agree with those previously reported by the USBM-Albany. Further conclusions drawn by CEGB were that the high affinity of alkalized alumina for water at low temperatures was not present in the reaction temperature range, the uptake of water having dropped to below 1% of the sorbent's weight at a temperature of 300°C. Similarly, the accumulation of chlorine compounds found in flue gases, which had given some cause for concern in bench-scale studies with simulated flue gases, was found to be negligible when actual flue gases were used. This is attributed to the catalytic effect of the nitrogen oxides, in that the sulfur trioxide is preferentially sorbed over the flue gas chlorides.

In an analysis of the available CEGB data typical sorbent loading vs. time curves were prepared by AVCO and are shown in Figure 36. When these results are compared to the USBM-Albany's sorbent loading vs. time curves shown in Figure 20, it can be seen that the CEGB loadings are about 62.5% of the Albany loadings at similar conditions. However, the Albany runs were made with a Grace sorbent whereas the CEGB runs were made with a Peter Spence sorbent and in independent studies by the AVCO Corporation, the Grace material was found to be approximately 30% more reactive in the loading range compared. If the CEGB results are scaled up by this factor, it can be seen that they agree quite well with the Albany results. In conclusion, the sorption effects and loadings reported by CEGB have been found to be in general agreement with the presently available U. S. data.

d. Sorption Modeling

(1) Kinetic Modeling

The following discussion was abstracted from two recent USBM-Albany reports (1). It is felt that this discussion

(1) USBM-Albany, Annual Report, June 30, 1969, pg. 4 and USBM-Albany, Progress Report, September, 1968, pp. 2 and 3.

adequately summarizes the present state of the art in the area of kinetic modeling.

Initial studies to determine the reaction rates for sorption and regeneration have been concerned with the development of a mathematical model for sorption rate based on batch thin bed studies. Results of these studies are shown in Figure 37, wherein the four equations currently being used are adjusted to fit the loading data for Grace No. 1 sorbent at 300°C without NO_x. The four equations which are compared are:

1. $yt = 22.5 \ln \left(1 - \frac{\mu}{0.16} \right)$, which was used by Amundson in his studies of adsorption (Amundson, Neal R., "Mathematics of Adsorption in Beds," J. Phys. Colloidal Chemistry, v. 52, 1948, pp. 1153-7);
2. $yt = 3,000 \mu^2 + 65 \mu$, the tarnish equation presented in Jost (Jost, W, "Diffusion in Solids, Liquids, Gases," Academic Press, Inc., New York, 1952, pp. 352-354, with truncation at saturation);
3. $yt = 691 \left[1 - \left(1 - \frac{\mu}{0.16} \right)^{2/3} \right] - 2,815 \mu$, which was developed by AVCO (Removal of SO₂ from Flue Gas," Final Report, Contract No. PH 86-67-51, November 1, 1967, pp. 61-100);
4. $yt = [154 \ln \left(1 - \frac{\mu}{0.16} \right) - 895 \mu]$, a modification of the Amundson equation which provides an identical fit to the other equations at low loads;

where μ = sulfur loading on the sorbent, lbS/lb sorbent

t = time, minutes

y = SO₂ composition of the gas, % vol

Although the scatter of the data is too great to allow a definite choice among the models, some definite observations can be made. The Amundson equations appear not to fit as

BETTER ROAD 42186

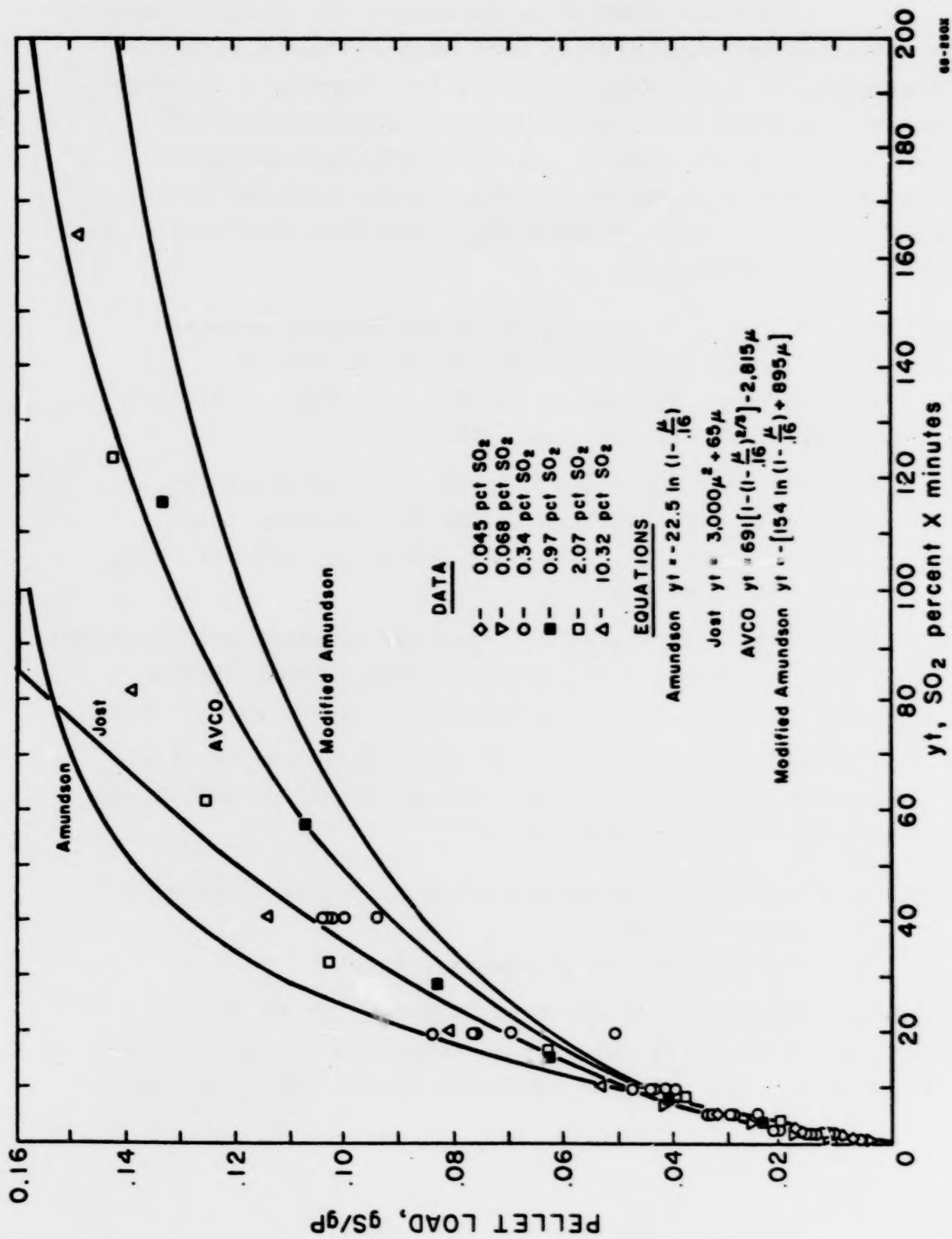


FIGURE 37 - Comparison of Loading Equations at 300° C

well as the others, although fitting to the data at higher loads would reduce the error. At the highest loads the AVCO equation obviously fits best, but at intermediate loads, the Jost equation appears to be better than the AVCO equation. In the loading range of 0-10 percent sulfur, which is the range of principle interest, the Jost equation fits best while in the 0-5% range all of the equations give essentially identical results. However, the Amundson equation is the easiest to handle while the AVCO equation is the most difficult. As such, the Amundson equation has been used almost exclusively as the rate expression in sorption modeling.

(2) Fixed-Bed Modeling

A theoretical model representing the sorption of SO_2 in fixed beds of alkalized alumina was derived by the USBM-Bruceton. The derivation of this model is contained in Appendix D of this report.

To determine the effect of changes in system parameters, a computer program was developed utilizing the Bruceton sorption model. A sample output from this program is shown in Table 22. The output data lists the gas velocity, bed pressure drop, and number of stages for an input range of bed heights and column diameters. The number of stages are the number of parallel fixed beds required for sorption at the input conditions. The output was arranged in this fashion for convenience but the results may be combined with the column diameter to give the effective cross sectional area required for sorption for configurations other than cylindrical.

Because the bench-scale studies at Albany and AVCO used relatively small ratios of sorbent to SO_2 , the inlet and exit SO_2 concentrations were essentially the same. Therefore, the data they obtained could not be compared to the

TABLE 22

DETERMINATION OF MULTIPLE FIXED-BED PARAMETERS
BASED ON U. S. BUREAU OF MINES FIXED-BED MODEL

Assumed Time for Effluent Gas to Reach 10% of
the Inlet Gas Concentration (i.e., cycle time):
24 hours

INPUT VARIABLES

Gas Flow Rate (Appendix I)	61150	CFS
Initial Gas Composition	0.0035	Lb. SO ₂ /lb. flue gas
Sorbent Loading at Sat'n.	0.1920	Lb. SO ₂ /lb. sorbent
Rate Constant	25.00	1/hr.
Temperature	625	°F
Viscosity	0.03	CP (Centipoises)
Gas Density	0.0383	Lb./ft. ³
Solid Bulk Density	42.00	Lb./ft. ³
Void Fraction of Bed	0.5	Dimensionless
Particle Diameter	0.06	Inches

OUTPUT

<u>Bed Height</u> <u>(Ft.)</u>	<u>Col. Dia.</u> <u>(Ft.)</u>	<u>Gas Vel.</u> <u>(Ft/Sec)</u>	<u>ΔP</u> <u>(In. H₂O)</u>	<u>No. Stages</u>
1	20	0.58	0.95	335
2	20	1.16	4.21	109
1	30	0.58	0.95	149
3	30	1.74	10.44	49
1	40	0.58	0.95	83
3	40	1.74	10.44	27

theoretically based Bruceton fixed bed model. Although this model has not been confirmed by experimental results, as were the fluid bed and dispersed phase models, it has been used to design the commercial scale fixed bed unit, for it is the only available tool for that purpose.

(3) Fluid-Bed Modeling

In the area of fluid bed sorption, two sorption models have been proposed. The first model, a theoretical one, has been presented by the USBM-Albany. The second model, an empirically derived one, was presented by CEGB.

The rate constant used in the USBM-Albany model is derived from the experimental data shown in Table 10 as follows:

- An integrated form of the Amundson equation is used
- $$r = \frac{d\mu}{dt} = ky \left(1 - \frac{\mu}{\mu_s}\right)$$

where k = rate constant

μ_s = sorbent loading at saturation

μ_o = initial sorbent loading

rearrange, $\frac{d\mu}{1 - \frac{\mu}{\mu_s}} = Kydt$

$$\int_{\mu_o}^{\mu} \frac{d\mu}{\left(1 - \frac{\mu}{\mu_s}\right)} = Ky \int_0^t dt$$

integrate,

$$-\mu_s \ln \left(1 - \frac{\mu}{\mu_s}\right) + \mu_s \ln \left(1 - \frac{\mu_o}{\mu_s}\right) = Kyt$$

simplify,

$$\mu = \mu_s - (\mu_s - \mu_o) e^{-\frac{Kyt}{\mu_s}} \quad (1)$$

• Since sorbent loading (μ) versus time (t) data are available from Table 10, equation (1) may be evaluated for μ_s , μ_e , and K using least squares estimation of non-linear parameters. Such a technique has been developed (Marquardt, D. W., "An Algorithm for Least Squares Estimation of Non-linear Parameters", J. Soc. Indust. and Appl. Math., 11 No. 2, (1963) 431-441) and the program is available from the "Share Program Library".

• Using all 29, 300°C data points from Table 10, the following values are obtained:

$$K = 0.00794 \text{ min}^{-1}$$

$$\mu_s = 0.1637 \text{ lbs sulfur lb sorbent}$$

$$\mu_e = 0.0066 \text{ lbs sulfur lb sorbent}$$

• As a check on the calculated value of K , it was compared to that reported in Figure 37. The Amundson equation shown in Figure 37 is

$$yt = -22.5 \ln \left(1 - \frac{\mu}{0.16} \right)$$

$$\text{where } \frac{-\mu_s}{K} = -22.5 \text{ and } \mu_s = 0.16$$

therefore, $K = 0.0071 \text{ min}^{-1}$ which is a good check on the calculated value of 0.00794 shown above.

To compare these models, the required sorbent bed heights were calculated by each of these models for various exit sulfur loadings, sample calculations are shown in Tables 23 and 24. The results of these calculations are shown in Table 25 and indicate that the two models produce results that are in good agreement but with the Blyth model being more sensitive to sorbent loading than the Albany model.

TABLE 23

SAMPLE CALCULATION OF FLUID BED SORBENT INVENTORY

USING THE USBM-ALBANY MODEL

$$\frac{w}{y_o W} = \frac{k}{\mu_s} \cdot \frac{\bar{y}}{y_o} \left(1 - \frac{\bar{y}}{y_o} \right) / \left[\left(\frac{50 W k}{M G} + 1 \right) \frac{\bar{y}}{y_o} - 1 \right]$$

where:

- G = Gas flowrate, ft³/min. = 3,720,100
- k = Reaction rate constant = 0.00794
- M = S content of SO₂, gm S/ft³ SO₂
- w = Rate of sorbent addition, gm sorbent/min
- W = Weight of sorbent in the bed, gms
- y_o = SO₂ concentration in gas at inlet, volume %, = 0.2146
- $\bar{y}$ = Arithmetic average SO₂ concentration in gas, volume %, = 0.11803 @ 90% SO₂ removal
- μ_s = Maximum of saturation S load on the sorbetnt = 0.1407 gm S/gm P

Basis: 6% sulfur at exit, based on total solids weight

SULFUR LOADING @ INLET, μ

μ = 2.6 wt % S = Average sorbent loading at inlet; assumed, based on USBM-Bruceton data for X-3F & 423 X-4E sorbents

SULFUR LOADING @ EXIT, $\langle \mu \rangle$

$$\langle \mu \rangle = \frac{6.0 \text{ lbs}}{100 \text{ lb total weight}}$$

SULFUR BALANCE for 100 lbs of sorbent feed

Let x = lb S picked up from flue gas

Continued

TABLE 23 (Con't)

If sorption occurs as SO_3

$$\frac{\text{lb SORBED}}{\text{lb SULFUR}} = \frac{1 \text{ MOL } \text{SO}_3}{1 \text{ MOL S}} \cdot \frac{80.064 \text{ lb } \text{SO}_3}{\text{MOL } \text{SO}_3} \cdot \frac{\text{MOL S}}{32.064 \text{ lb S}}$$

$$= \frac{2.497 \text{ lb } \text{SO}_3}{\text{lb S}}$$

$$\therefore \text{wt gain} = 2.497 x$$

By material balance

$$\frac{\text{SULFUR @ INLET} + \text{SULFUR GAINED}}{\text{TOTAL WT @ INLET} + \text{TOTAL WT GAINED}} = \frac{\text{SULFUR @ EXIT}}{\text{TOTAL WT @ EXIT}}$$

$$\text{OR} \quad \frac{100\mu + x}{100 + 2.497 x} = <\mu>$$

$$\frac{2.6 \#S + x \#S}{100 + 2.497 x} = 0.06$$

$$\therefore x = 3.999 \# \text{ Sulfur sorbed per } 100\# \text{ sorbent feed}$$

SULFUR BALANCE FOR GAS STREAM

$$y_o = 0.2146\% \text{ SO}_2 \text{ (MWK Progress Report \#3)}$$

$$y_e = 0.1 y_o$$

$$G = 288,583 \frac{\text{mol flue gas}}{\text{hr}} \text{ (MWK Progress Report \#3)}$$

$$\Delta \text{SO}_2 = G(y_o - y_e) = G(0.9y)$$

$$\Delta \text{SO}_2 = 288,583 \frac{\text{mol f.g.}}{\text{hr}} \cdot 0.0019314 \frac{\text{mol SO}_2}{\text{mol f.g.}} = 557.37 \text{ mol SO}_2/\text{hr}$$

$$\Delta S = 557.37 \frac{\text{mol SO}_2}{\text{hr}} \cdot \frac{1 \text{ mol S}}{\text{mol SO}_2} \cdot 32.064 \frac{\text{lb S}}{\text{mol S}}$$

$$\Delta S = 17871 \frac{\text{lb S}}{\text{hr}}$$

Continued

TABLE 23 (Con't)

SORBENT FEED RATE, W

$$w = 17871 \frac{\text{lb S}}{\text{hr}} \cdot \frac{100 \text{ lb Sorbent Feed}}{3.99 \text{ lb S sorbed}}$$

$$w = 446,887 \frac{\text{lb Sorbent Feed}}{\text{hr}} = 3,381,445 \frac{\text{gm}}{\text{min}}$$

AVERAGE SO₂ CONCENTRATION, $\bar{y}$

$$\bar{y} = \frac{y_o}{2} \left(1 + \frac{y_e}{y_o} \right) = \frac{0.2146}{2} \left(1 + \frac{0.1y_o}{y_o} \right)$$

$$\bar{y} = 0.11803\% \text{ SO}_2$$

WT OF S PER UNIT VOLUME SO₂, M

$$M = \left(\frac{1 \text{ MOL S}}{\text{mol SO}_2} \right) \left(\frac{32.064 \text{ lb S}}{\text{mol S}} \right) \left(\frac{\text{mol SO}_2}{359 \text{ ft}^3 \text{ SO}_2} \right) \left(\frac{492^\circ \text{R}}{1060^\circ \text{R}} \right) \left(\frac{454 \text{ gms}}{\text{lb}} \right)$$

$$M = 18.82 \frac{\text{gm S}}{\text{ft}^3 \text{ SO}_2}$$

Substitute the above vlaues into the USBM model to find sorbent inventory W

$$\frac{3,381,500}{0.2146 W} = \frac{0.00794 \cdot 0.11803}{0.1407 \cdot 0.2146} 1 - \left(\frac{0.11803}{0.2146} \right)$$

$$\left[\left(\frac{50 \cdot W \cdot 0.00794}{18.78 \cdot 3,720,100} + 1 \right) \frac{0.11803}{0.2146} - 1 \right]$$

$$W = 201,583,000 \text{ gms sorbent}$$

$$\text{or } W = 444,000 \text{ lbs sorbent}$$

TABLE 24

CALCULATION OF SORBENT BED HEIGHT USING THE C.E.G.B.-BLYTH MODEL

$$\log_{10}(1-\frac{w}{b}) = -m (\frac{ct}{d} + n)$$

where b = function of temperature = 9.0 @ T = 330°C
 n = constant = 0.13
 m = constant = 0.22
 w = S concentration, @ time = t, minus the inlet or residual S concentration, lbs/100 lb sulfur free sorbent
 c = log mean SO₂ concentration in flue gas, mol fraction
 t = sorption time, min.
 d = particle diameter = in = 0.0359 in. (1)
 L = feed rate of solids by material balance = 446,887 lb/hr (2)

Basis: S on loaded sorbent = 6 wt %
 S on regenerated sorbent = 2.6 wt %

Assume sorption occurs as SO₃

$$\text{Total weight gain} = \#S \text{ sorbed} \times \frac{MWSO_3}{MWS} = \#S \times \frac{80.064}{32.064}$$

$$= 2.497 \times \#S$$

Inlet: wt S = 2.6%; total wt = (2.6)(2.497) = 6.4922
 and sulfur-free-sorbent (S-F-S) = 100 - 6.4922 = 93.5078%

$$\frac{2.6}{93.5078} \times 100 = 2.7805\%S/100\%S-F-S$$

$$\text{Outlet: } \frac{X}{93.5078+2.497X} = 0.06$$

$$X = 6.5992\%S$$

$$\text{and } \frac{6.5992}{93.5078} \times 100 = 7.0574\%S/100\%S-F-S$$

$$\therefore, w = 7.0574 - 2.7805 = 4.2769\%S/100\%S-F-S$$

$$\text{@ 90\% removal } C = \frac{C_1 - C_2}{\ln \frac{C_1}{C_2}} = \frac{0.002146 \text{ mol SO}_2 \text{ in} - 0.0002146 \text{ mol SO}_2 \text{ out}}{\ln \frac{0.002146}{0.0002146}}$$

$$C = 0.0008388 \frac{\text{mol SO}_2}{\text{mol flue gas}}$$

TABLE 24 (Con't)

Substituting into the Blyth Model

$$\log_{10} \left(1 - \frac{4.2769}{9.0} \right) = -0.22 \left(\frac{0.0008388t}{0.0359} + 0.13 \right)$$

$$t = 48.91 \text{ min}$$

@ average residence time of 48.91 min., the bed inventory is:

$$\text{Inventory} = L \cdot t = 446,887 \text{ lb/hr} \cdot \frac{48.91 \text{ min}}{60 \text{ min/hr}}$$

$$\text{Inventory} = 364,287 \text{ lb solids}$$

Since @ 40' dia. 10 beds are required.

$$\text{Inventory per bed} = 36429 \text{ lb solids}$$

@ 45 lb/ft³, solids density & 40' dia. bed

$$\text{Settled bed ht.} = \frac{36429 \text{ lb solids}}{45 \frac{\text{lb}}{\text{ft}^3} \cdot \frac{\pi}{4} \cdot (40 \text{ ft})^2}$$

$$\text{Settled bed ht.} = 0.644 \text{ ft}$$

-
- (1) Weight mean average calculated from data in Table 4, USBM-Bruceton, Quarterly Report, June 30, 1968.
 - (2) Table 23, this report.

TABLE 25

A COMPARISON OF THE BED HEIGHTS REQUIRED FOR
FLUID BED SORPTION AS PREDICTED BY THE USBM-
ALBANY, AND C.E.G.B. - BLYTH MODELS

<u>EXIT SORBENT LOADING, %S</u>	<u>USBM-ALBANY MODEL BED HEIGHT¹</u>	<u>CEGB BLYTH MODEL BED HEIGHT¹</u>
	(ft)	(ft)
6	0.785	0.644
7	0.905	0.872
8	1.080	1.38

¹ For ten 40' Diameter Reactors

Although a direct comparison of these models is not quite valid in a theoretical sense (the temperature in the CEGB model was 626°F whereas the temperature used in the Albany model was 600°F), the good agreement of these models (within 0.3 ft. on bed height) indicates that either should be adequate for design purposes.

The vessel heights in the proposed commercial fluid bed unit will be set by criteria other than sorption (e.g., disengaging height above the bed). Therefore, the good agreement between the theoretical and empirical models indicates that sorption in the commercial unit may be calculated by the easy to use empirical model rather than the more tedious theoretical one, once this theoretical model has been verified by comparison with pilot plant results.

This verification has been provided by the data in Tables 13 and 14 from the USBM-Albany testing program. Figure 38 compares the calculated and measured extraction as indicated by both gas and pellet analysis to that predicted by the theoretical model. Although the data exhibit a good deal of scatter, some of which is most likely due to difficulties in measurement and sampling, the relative agreement of the pilot plant data with the sorption model can be seen. The average exit sorbent loading obtained in these tests was 0.072 grams of sulfur per gram of particle. At this exit loading the Albany model predicts that for 90% removal, a bed height of about 11 inches is required (see Table 25). The bed heights which were used in this testing program ranged from 5.5 to 6.8 inches and with a gas velocity of about 2.7 to 3.2 ft/sec, gave an average sulfur removal of 90.2%, thus verifying the proposed sorption models.

(4) Dispersed Phase Modeling

An empirical model to predict the sorption of

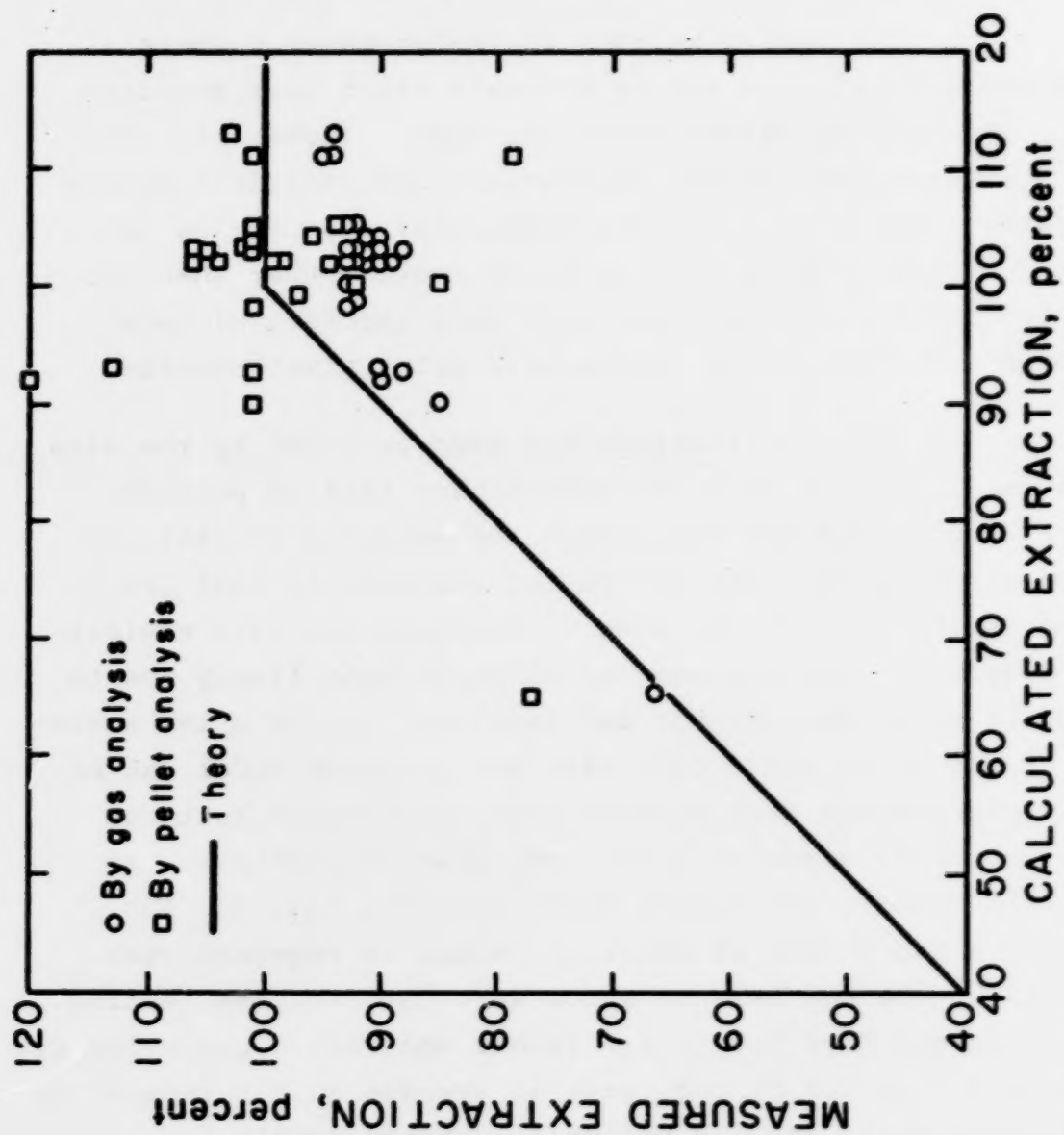


FIGURE 38 - Comparison of Calculated and Measured Extraction, Long Run

68-100

SO₂ in a dispersed phase system was developed by the USBM-Bruceton, based on their pilot plant studies. A derivation of this model is contained in Appendix E.

Experimental validation of this model has not been conclusive due to the scatter exhibited by much of the pilot plant data. A specific example of this variability can be seen when the average sulfur loadings from the C and D and E and F runs, which were presented in section 2-C-(3) of this report, are plotted vs. ratio of the sorption rate to the SO₂ composition of the flue gas.

If the sulfur loading expression is represented in the form

$$\frac{\bar{r}}{y} = K \frac{(x_o + x_f)^m}{2}$$

where: $\bar{r}$ = average sorption rate, hr⁻¹
 y = gas SO₂ concentration, mol fraction
 K = rate constant, hr⁻¹
 x_o = sulfur concentration of the feed sorbent, lbs/lb sorbent
 x_f = sulfur concentration of the exit sorbent, lbs/lb sorbent,

then the exponent, m , may be obtained from the slope of a log-log plot of the data as was done in Figures 39 and 40 for test series C, D, E, and F, respectively. The results of these plots indicate that for the C and D test series the value of m is + 2/3, while the value of m obtained from the E and F series test data is -2/3. Statistically, the regression equation for the C and D test series runs is above the level required for significance if test run D-115 is

FIGURE 39

$\text{Log}_e (\bar{r}/y)$ VS $\text{Log}_e \left[\frac{(x_0 + x_f) \cdot 10^3}{2} \right]$

(TEST SERIES C AND D)

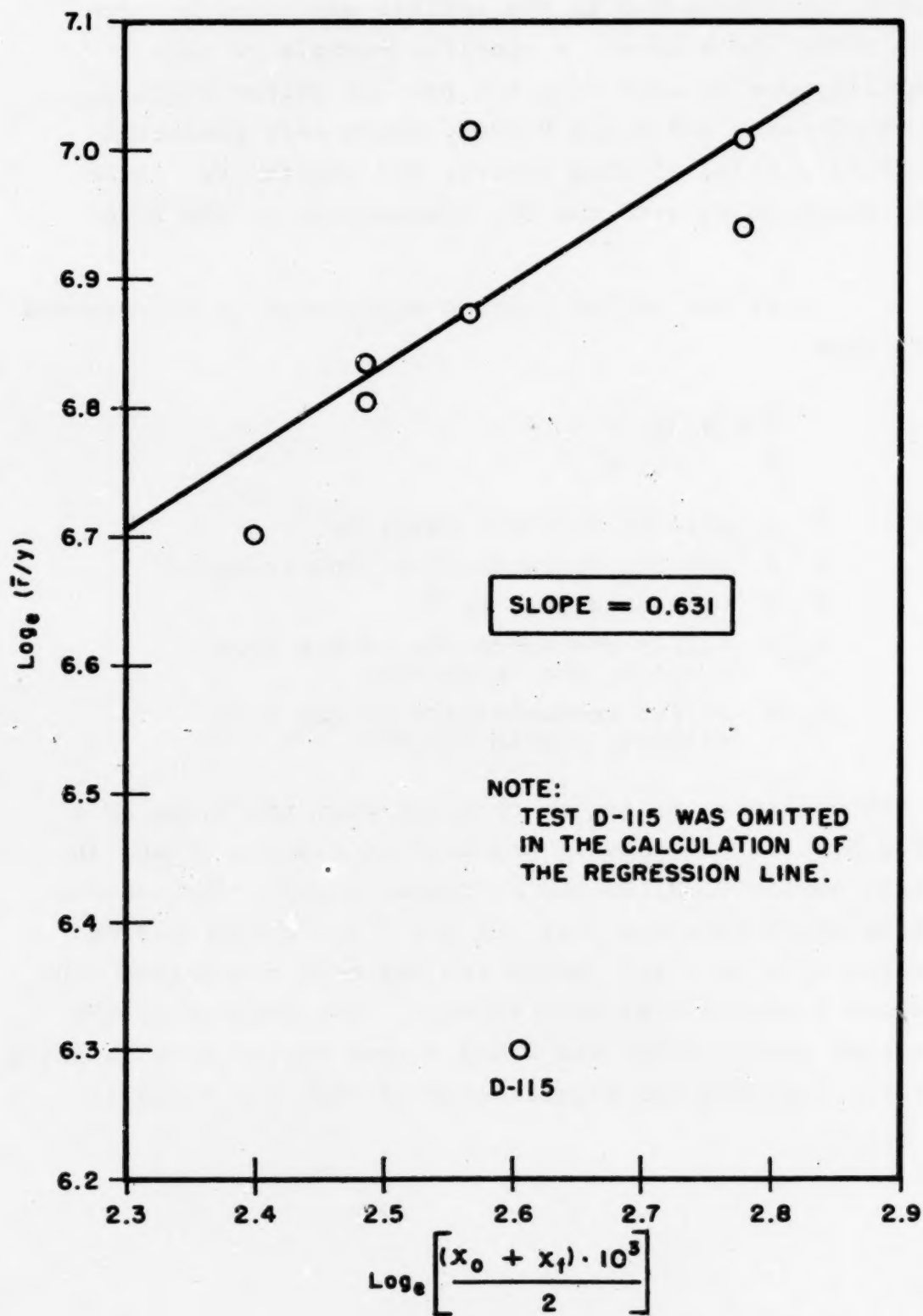
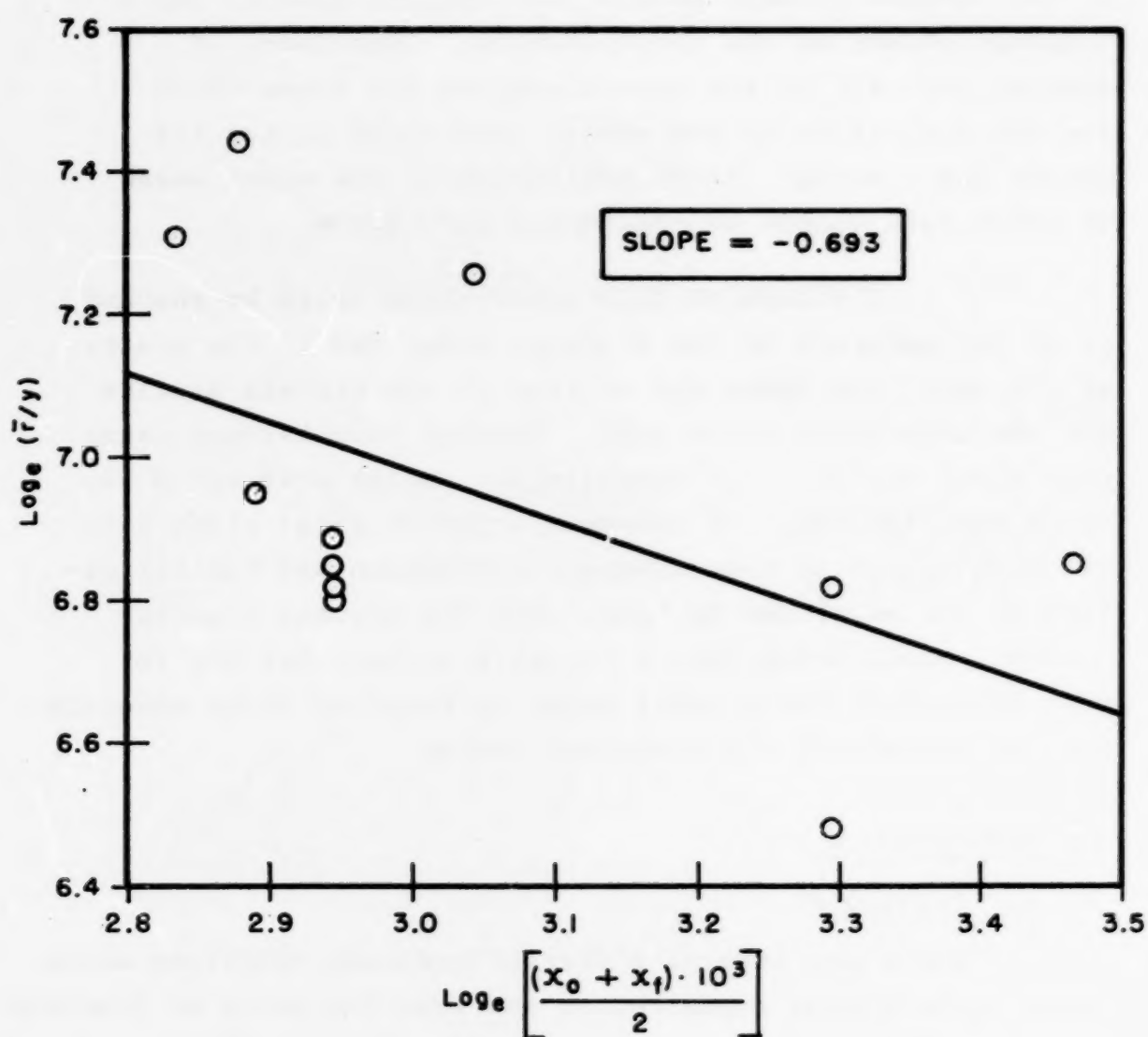


FIGURE 40
 $\text{Log}_e (\bar{r}/y)$ VS $\text{Log}_e \left[\frac{(x_0 + x_f) \cdot 10^3}{2} \right]$

(TEST SERIES E AND F)



omitted from the data. For the test series E and F runs, however, the correlation coefficient of the regression equation is 0.43, which is well below the required level for significance. Furthermore, if the two groups of test data are combined, the resultant slope of the regression equation approaches zero, which in essence indicates that the effect of sorbent loading on sorption is negligible. This last result is highly unlikely for it has been shown by the various kinetic models that sorbent loading has a distinct effect on the sorption rate. Therefore, it appears that all of the data presented for these tests are not indicative of the actual conditions in the dispersed phase sorber; thus, evaluation of the model based on these data cannot be considered conclusive.

Although no firm conclusions could be reached as to the accuracy of the Bruceton model due to the scatter of the data, the model was applied in the process studies for the commercial scale unit. Typical calculations using this model are given in Appendix G, Tables G-89 and G-92. It is expected that, if necessary, future pilot plant data can be obtained so that adequate evaluation and validation of the model can be made. For the present studies, however, considering that a suitable sorbent has not yet been developed, the present model is believed to be adequate for the commercial scale reactor design.

3. Regeneration

a. Reactions

There are several different possible reactions which could occur during regeneration and thus the heats of reaction could vary widely depending on which of the reactions are

actually involved. Heats of reaction reported in the literature, MWK's calculated heats of reaction, and heats of formation for the various reactions and compounds are shown in Tables 26 and 27.

As can be seen from the tabulated data in Table 26, there is a considerable discrepancy in the MWK vs. CEGB calculated heat of reaction for equation 2. Also, depending on which of the several equations is the actual valid one, the reaction could be endothermic or exothermic and the heat of reaction could have a significant effect on the regenerator heat balance. For example, USBM has reported a 150°F temperature increase in fixed bed regeneration with reformed natural gas in the 55,000 CFH pilot plant.

b. Status of Data

(1) USBM-Bruceton Studies

(a) 55,000 CFH Pilot Plant Results

1 - Fixed Bed Regeneration

USBM reports for the case of fixed bed regeneration with reformed natural gas in the large pilot plant (Pittsburgh Progress Report - Sec I - 12/31/67), at a space velocity range of 15-20 hr⁻¹ and temperatures from 1175-1250°F, an overall utilization of 75% of the reducing gas for a sorbent sulfur content reduction from 2.5 wt % to 0.9 wt % in 10 hours.

2 - Moving Bed Regeneration

For the case of continuous gravitating bed regeneration with reformed natural gas in the large pilot plant (Pittsburgh Progress Report - Sec I - 3/31/68), USBM reports that even at lower than optimum temperature, the reaction proceeded readily, with little additional sulfur removal after 2-1/4 hours. For an average of 24 sets of data taken

TABLE 26

VARIOUS REGENERATION REACTIONS

EQUATION	ΔH_r (K cal/g mole)		
	77°F (25°C)	1200°F (649°C)	
	MWK	MWK	
REDUCTION WITH H_2			
1) $Na_2SO_4 + 4H_2 \rightarrow Na_2O + H_2S + 3H_2O$	52.8	52.5 ¹	44.9
2) $Na_2SO_3 + Al_2O_3 + 3H_2 \rightarrow 2NaAlO_2 + H_2S + 2H_2O$	-1.81	-23.3 ²	-11.7
3) $Na_2SO_4 + Al_2O_3 + 4H_2 \rightarrow 2NaAlO_2 + H_2S + 3H_2O$	9.7		0.83
REDUCTION WITH CO			
4) $Na_2SO_4 + 4CO + H_2O \rightarrow 4CO_2 + H_2S + Na_2O$	13.5		12.6
5) $Na_2SO_3 + Al_2O_3 + 3CO + H_2O \rightarrow 3CO_2 + H_2S + 2NaAlO_2$	-31.3		-35.8
6) $Na_2SO_4 + Al_2O_3 + 4CO + H_2O \rightarrow 4CO_2 + H_2S + 2NaAlO_2$	-29.7		-31.3

1 AVCO Thermochemical Calculations.

2 CEGB, Dec. 1965 - Bomb Calorimetry and Thermochemical Calculations

TABLE 27

HEATS OF FORMATION AT 25°C (K cal/g mole)

COMPOUND	SOURCE			
	(1)	(2)	(3)	(4)
$\text{Na}_2\text{SO}_4(\text{c})$	-330.50	-330 + -331.55	-327.4	-330.90
$\text{Na}_2\text{SO}_3(\text{c})$	-261.2		-260.4	-260.6
$\text{Na}_2\text{O}(\text{c})$	- 99.45			- 99.4
$\text{Al}_2\text{O}_3(\text{c})$	-399.09	-400.4		
$\text{NaAlO}_2(\text{c})$		-270.84	-272.88	
$\text{CO}(\text{g})$	- 26.416			
$\text{CO}_2(\text{g})$	- 94.052			
$\text{H}_2\text{S}(\text{g})$	- 4.77			- 4.82
$\text{H}_2\text{O}(\text{g})$	- 57.80			

(1) Perry, "Chemical Engineers Handbook", 4 ed., 1963

(2) "JANAF Thermochemical Data" Tables

(3) "International Critical Tables" - (Data at 18°C)

(4) National Bureau of Standards-Circular 500 - "Selected Values of Chemical Thermodynamic Properties"

during 2 days of steady state operation, feed and exit gas composition and flow rate for a temperature range of 1100-1150°F and a sorbent feed rate of 150 lbs/hr are tabulated in Table 28. Overall reducing gas utilization was 50% for a sorbent sulfur content reduction from 2.7 wt % to 0.9 wt % in 2-1/4 hours. USBM states that stepwise reduction occurs during regeneration; this was reinforced by chemical analyses of sorbent samples taken from bed heights corresponding to different residence times. Longer residence times indicated higher sulfide concentrations with the remainder of the sulfur present as sulfate--no sulfite was detected. Table 28 indicates that the sulfur removed from the absorbent is equivalent to 1.33 times the H_2S recovered. USBM states that this may be due to sample loss or elemental sulfur formation in the regenerator and therefore filters have been installed in the exit line. It is also reported that an overall material balance does not account for 3.5% of the carbon present in the reformed natural gas feed. Visual examination of the regenerator revealed carbon deposition only at locations where stainless steel probes protruded into the vessel. The quantity of the deposited carbon was not reported but it was quite small.

(b) Bench-Scale Tests With Various Reducing Gases

In decreasing effectiveness, (amount of sulfur removal) the reducing gases used for regenerating the spent absorbent are reformed natural gas, hydrogen, producer gas, and methane. According to USBM, the minimum temperature for reformed natural gas is 1200°F. Data are presented in Table 29 from which the following conclusions can be made:

- Complete regeneration was achieved with H_2 at 1250°F, assuming an initial sulfur concentration of about 1%.
- Regeneration with reformed natural gas resulted in a lower sulfur concentration than with H_2 .

TABLE 28
OPERATING CONDITIONS DURING CONTINUOUS REGENERATION

(TEST NO. G1)

Temperature, °F 1100 to 1150
Sorbent Feed Rate, lb/hr 160

GAS COMPOSITION AND FLOW RATE	COMPOSITION (VOL PCT)	RATE (LB MOLE/HR)
Reformed natural gas:		
H ₂	74.2	0.592
CO	15.8	.126
CO ₂	10.0	.079
Regenerator exit gas:		
H ₂	40.1	0.313
CO	7.6	.059
CO ₂	17.2	.134
CH ₄	0.6	.005
H ₂ S	8.0	.063
H ₂ O	26.5	.207

SORBENT SULFUR LOADING

RESIDENCE TIME (HR)	SULFUR (WT PCT)	RATE (LB MOLE/HR)
0 (inlet)	2.66	0.133
2.25	0.88	---
4.50 (exit)	.74	.037

Three cycles of absorption-regeneration were completed.

These represent an average of 24 sets of data taken during two days of steady-state operation.

REF: USBM-Pittsburgh-Sec. I
3/31/68 Quarterly Report - Table 1

TABLE 29
REDUCTION OF SPENT ALKALIZED ALUMINA (21 PCT Na) WITH REDUCING GASES

LENGTH OF TEST, 4 HR
HOURLY SPACE VELOCITY, 100 HR⁻¹

Temperature, °F	Hydrogen		Methane		Reformed Natural Gas ¹		Producer Gas ²	
1200	2.3	1.1	2.3	1.6	2.3	0.6	2.3	1.2
	6.9	2.5					6.9	4.0
1250	2.3	0.9						
	6.9	1.1						
1290	2.3	0.9	2.3	1.6	2.3	0.4	2.3	0.9
	6.9	1.1					6.9	1.9

- ¹ 77 pct H₂, 13 pct CO, 10 pct CO₂.
- ² 14 pct H₂, 30 pct CO, 4 pct CO₂, 50 pct N₂, 2 pct CH₄.
- ³ Figures denote weight percent sulfur at start and end of test

REF: USBM, RI 7021
July 1967
Table 5, p. 31

- Regeneration with CH_4 was incomplete. Based on a limiting value of 0.9%, equivalent to 100% regeneration, 50% recovery of the sulfur was obtained with CH_4 after 4 hours at 1200°F and 1290°F.
- With the sorbent containing 2.3% S and based on a final sulfur value of 0.9%, complete regeneration was obtained at 1290°F with producer gas flowing for 4 hours at a space velocity of 100 hr^{-1} . At 1200°F, 80% sulfur removal was obtained. With the higher sulfur content of 6.9%, reduction to 0.9% was accomplished at 1290°F in 4 hours, by increasing the hourly space velocity from 100 to 200.

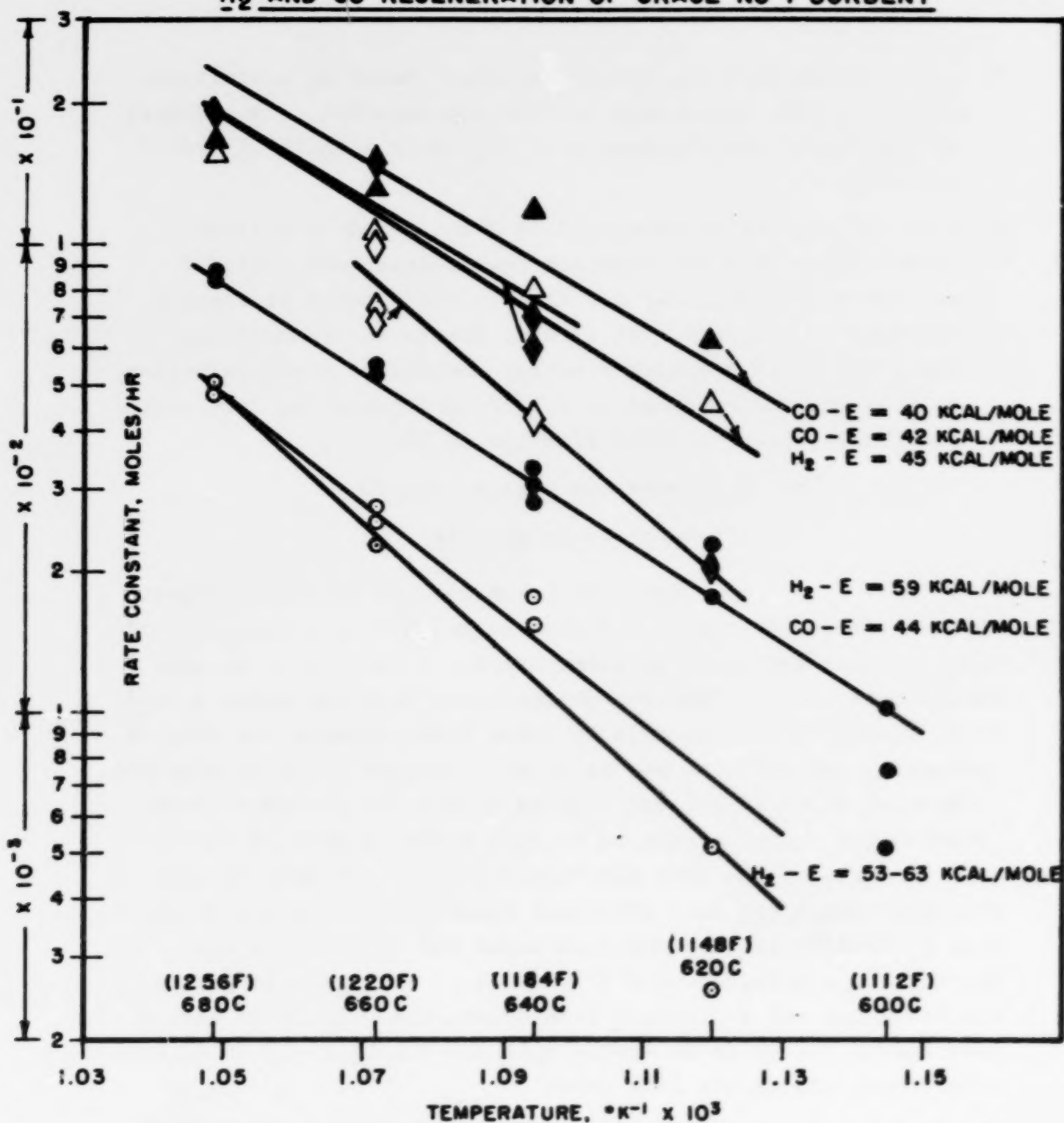
(c) Regenerations with H_2 and CO

1 - Bench Scale Results

USBM Pittsburgh Sec. II Quarterly Report of 12-31-67 states that the regeneration rate is independent of flow rate but dependent on temperature. A tabulation of some bench-scale results (Pittsburgh Quarterly 3-31-68) using H_2 and CO is listed in the Appendix in Table F-68, showing the rate of consumption of reducing gas as cc/min, assumed to be at standard conditions of 14.7 psia and 60°F as a function of temperature. Assuming the reaction rate to be zero order, a plot of these data in terms of the rate constant (reducing gas rate of consumption, moles/hr) vs. reciprocal absolute temperature should give a straight line on semi-log paper but the data do not exactly fit a straight line (Figure 41). If some data points are discarded and a straight line drawn, the calculated activation energy for CO is 44 kcal/g mole and for H_2 is 53 or 63 kcal/g mole, depending on the line drawn.

Based on the USBM tabulated data (Table F-68), CO reacts at a higher rate than H_2 but regeneration is incomplete; that is, residual sulfur content is high in comparison to that obtained in H_2 regeneration. For fines, however, the rate of reaction was not significantly different for CO or

FIGURE 4 I
ARRHENIUS PLOTS
H₂ AND CO REGENERATION OF GRACE NO I SORBENT



H ₂	CO	SOURCE OF DATA	INITIAL % S	ENERGY OF ACTIVATION, KCAL/MOLE	
				H ₂	CO
○	●	USBM PITTSBURGH QUARTERLY 3-31-68	2.5	53 - 63	44
△	▲	USBM PITTSBURGH QUARTERLY 9-30-68	9.8	45	40
◇	◆	USBM PITTSBURGH QUARTERLY 6-30-68	5.3	59	42

H₂. For a small particle radius it appears that only surface reactions occur and diffusion controlled reactions are not apparent.

2 - Regeneration of a Composite Sample from the Pilot Plant

A pilot plant composite sample of Grace No. 1, equivalent to the feed to the regenerator, was regenerated using H₂ and CO reducing gases. This alkalized alumina had a non-uniform size distribution (approximately .02 to .10 inch diameter) and contained an average sulfur content of 5.3 percent. A charge of 4.25 grams in the reactor occupied a 4cc volume and had a bed height of 8 mm. A flow of nitrogen was used while bringing the reactor up to temperature before the H₂ or CO was added. Appendix Table F-69 summarizes the results of regeneration at different temperatures.

One hour reduction tests with H₂ and with CO were compared at several temperatures and the overall percent of sulfur removal was determined. At temperatures of 620° and 640°C, the consumption of CO or H₂ was still going on after one hour, whereas at 660° and 680°C there was little, if any, consumption of reducing gas after 30 to 40 minutes. With hydrogen, the amount of sulfur removed increased as the temperature was increased but the CO experiments showed an inverse effect of temperature on the sulfur removal, even though the consumption rate of CO increased at higher temperatures. USBM stated that this could be due to the possibility of (1) a more stable sulfide formed at higher temperatures; (2) oxygen reaction favored at these temperatures; and (3) carbon deposition takes place at 660° and 680°C.

The maximum rates of consumption of the reducing gases tabulated in Table F-69 were converted to moles/hr and, assuming a zero order reaction rate, included as part of

Figure 41 (6-30-68 data). A least squares line was then drawn through the data points. These data predict higher regeneration rates but approximately similar energies of activation in comparison to the previously discussed 3-31-68 data of Figure 41.

Reducing gas mixtures of H_2 and CO were run using the same pilot plant composite sample. The last three tests in Table F-69 show the results of these experiments. H_2 and CO mixtures removed about as much sulfur as pure hydrogen. Regeneration with 2:1 and 1:2 mixtures of H_2 and CO gave practically the same percent sulfur removal over a one hour period at 640°C but the 1:2 H_2 :CO combination used less reducing gas to remove the same amount of sulfur. When a 1:1 ratio was used at 660°C, the sulfur removal was comparable to the 640°C tests.

One further feature of these H_2 and CO tests should be pointed out. The amount of water vapor formed during the regeneration reaction is decreased. USBM states that when using a 1:2 H_2 :CO mixture at 640°C, the quantity of water formed is only about a quarter of the amount of water formed during a H_2 regeneration at the same temperature. A regeneration gas of high CO content would reduce the amount of water vapor that contacts the sorbent at regeneration temperatures.

3 - Half-Hour Regeneration Tests

Pure H_2 and pure CO regeneration experiments were conducted using the original Grace sorbent (Grace No. 1) which was spent in the laboratory (9.8 percent sulfur and 1.0 percent carbon). Instead of the usual hour long test, the reaction time was reduced to a half-hour so that the regeneration would be incomplete and differences in the relative extent of sulfur removed could be demonstrated better as a function of the

reducing gas and the reaction temperature. Table F-70 in the Appendix lists the results of regenerations at various temperatures. H_2 consumption was completed after approximately a half-hour for the 660° and 680°C tests while at 620° and 640°C, it was still being consumed after one hour. H_2 regeneration at 680°C removed approximately three times as much sulfur as did CO regeneration at 680°C. The percent sulfur removal at 30 minutes varied from 82 percent at 680°C to 26 percent at 620°C for H_2 regeneration, whereas the CO regeneration removed approximately 30 percent sulfur at three temperatures (680, 660, and 640°C) and only 23 percent at 620°C. During the CO tests, the total consumption of the reducing gas and sorbent weight loss increased with reaction temperature. A few former runs using CO indicated an inverse effect of temperature on sulfur removal (Table F-69). The possibility of carbon deposition on the alkalized alumina causing high CO consumption without removing appreciable amounts of sulfur with increasing temperature was ruled out by the results of these half-hour tests. Carbon analyses did not indicate any increase above the one percent in the charge; in fact, the lowest CO reaction temperature showed the most carbon present. Oxygen removal is indicated.

Figure 41 also includes the data of Table F-70 considering the maximum rate (moles/hr) of consumption of reducing gas as the assumed zero order rate constant. A least squares line was drawn through the points (9-30-68 data). and the energy of activation for H_2 and CO calculated as shown on the plot.

In comparing the three sets of data plotted on Figure 41, those obtained for the case of an initial sulfur content of 9.8% indicated a higher reaction rate than those obtained for 5.3 and 2.5% sulfur. In every case CO reacted at a higher rate than H_2 but sulfur removal was incomplete; that is residual sulfur content is high in comparison to that obtained

in H_2 regeneration. It should be noted that the reaction rate constants plotted on Figure 41 are for an assumed zero order reaction. In any kinetic analysis for determining the order of reaction, concentration-time profiles are needed. The only information given in Tables F-68, F-69, and F-70 are rates of consumption of reducing gas and initial and final sulfur content. The rate of sulfur removal as a function of time is not included. It was observed in Table F-69, however, that 1:2 and 2:1 mixtures of H_2 :CO removed identical amounts of sulfur for the same maximum gas consumption rates. Since in a zero order reaction, the rate of change of any reactant is independent of the concentration of that reactant, this was assumed to be the case for H_2 and CO regeneration for each set of data. Therefore, Figure 41 is a plot of the rate constants, assumed to be moles/hr reducing gas consumption rate since the sorbent charge was the same for each test (maximum where specified from the appropriate tables), vs. reciprocal temperature on semi-log paper. These are Arrhenius plots for an assumed zero order reaction. Although there is a good deal of variation in the energy of activation calculated from the different sets of data, in all cases the reaction rate constant increases with temperature, indicating that the higher temperatures should improve regeneration.

(d) Albany Batch Regeneration Studies

1 - Data from Modified Thin Bed Test Unit

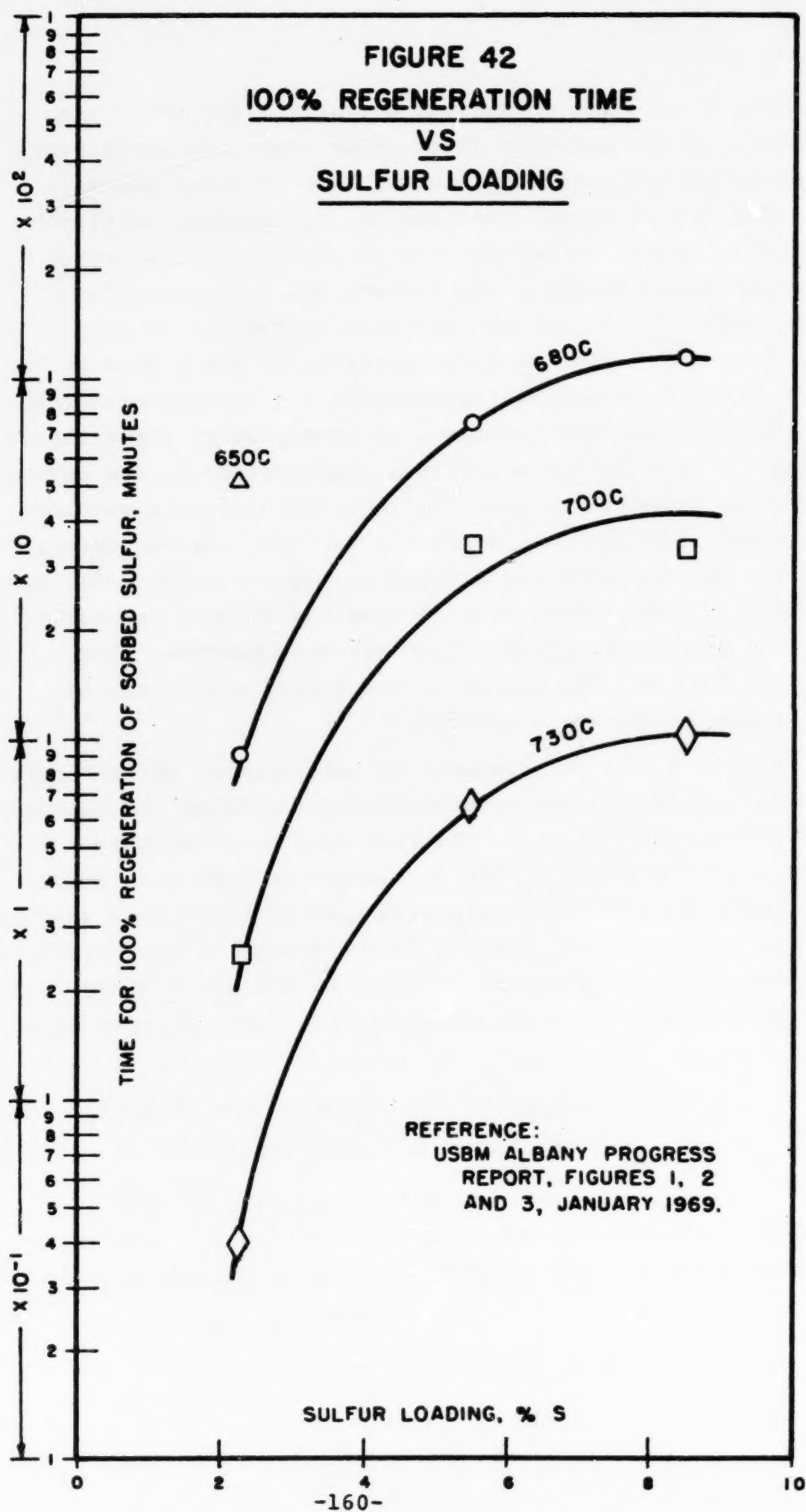
Batch regeneration tests with the modified thin bed test unit were carried out with simulated reformed reducer gas (50% N_2 , 10% CO_2 , 15% CO, 20% H_2 , and 5% H_2O). The results of these tests are tabulated in Appendix Table F-71. Figures F-79, F-80, and F-81 are plots of regeneration time vs. residual sulfur content with various temperature parameters on semi-log paper, for Grace No. 1 sorbents having an initial sulfur content of 8.5, 5.5, and 2.3% respectively. These plots

can be resolved into two relatively straight lines which seem to indicate that two parallel first order reactions are taking place. There is one rate-limiting reaction of principal interest. The second, slower reaction is not observed until the sulfur load is below the sulfur load of the original sorbent and this reaction represents the removal of residual sulfur. The first order rate constants tabulated in Table F-71 were obtained from the slopes of those portions of the curves of Figures F-79, F-80, and F-81 representing the removal of sorbed sulfur, the rate limiting reaction. A crossplot of these curves indicating the time required for 100% regeneration of the sorbed sulfur as a function of sorbent loading, for various parameters of temperature, is included as Figure 42. Calculated percent regeneration for all runs are plotted as Figures F-82, F-83, and F-84. The horizontal lines drawn across the figures represent the level at which all sorbed sulfur has been removed. The results show that at 730°C (1346°F) all sorbed sulfur can be removed in approximately 10 minutes.

The regeneration rate appears to be highly temperature dependent; as the temperature is reduced the regeneration rate drops very rapidly. The rate constants in Table F-71 drop from about 0.2 min^{-1} at 730°C (1346°F) to less than 0.005 min^{-1} at 650°C (1202°F). An Arrhenius plot of these rate constants (Figure 43) indicates that the activation energy is approximately 91 K cal/mole. In the temperature range of 650-700°C (1202-1292°F), a 10°C rise in temperature increases the regeneration rate by a factor of 1.66.

2 - Comparison of CEGB-Blyth Regeneration Model with USBM-Albany Data

A study was made comparing the CEGB-Blyth kinetic regeneration model to the USBM-Albany regeneration data discussed above. The Blyth model relates the regeneration



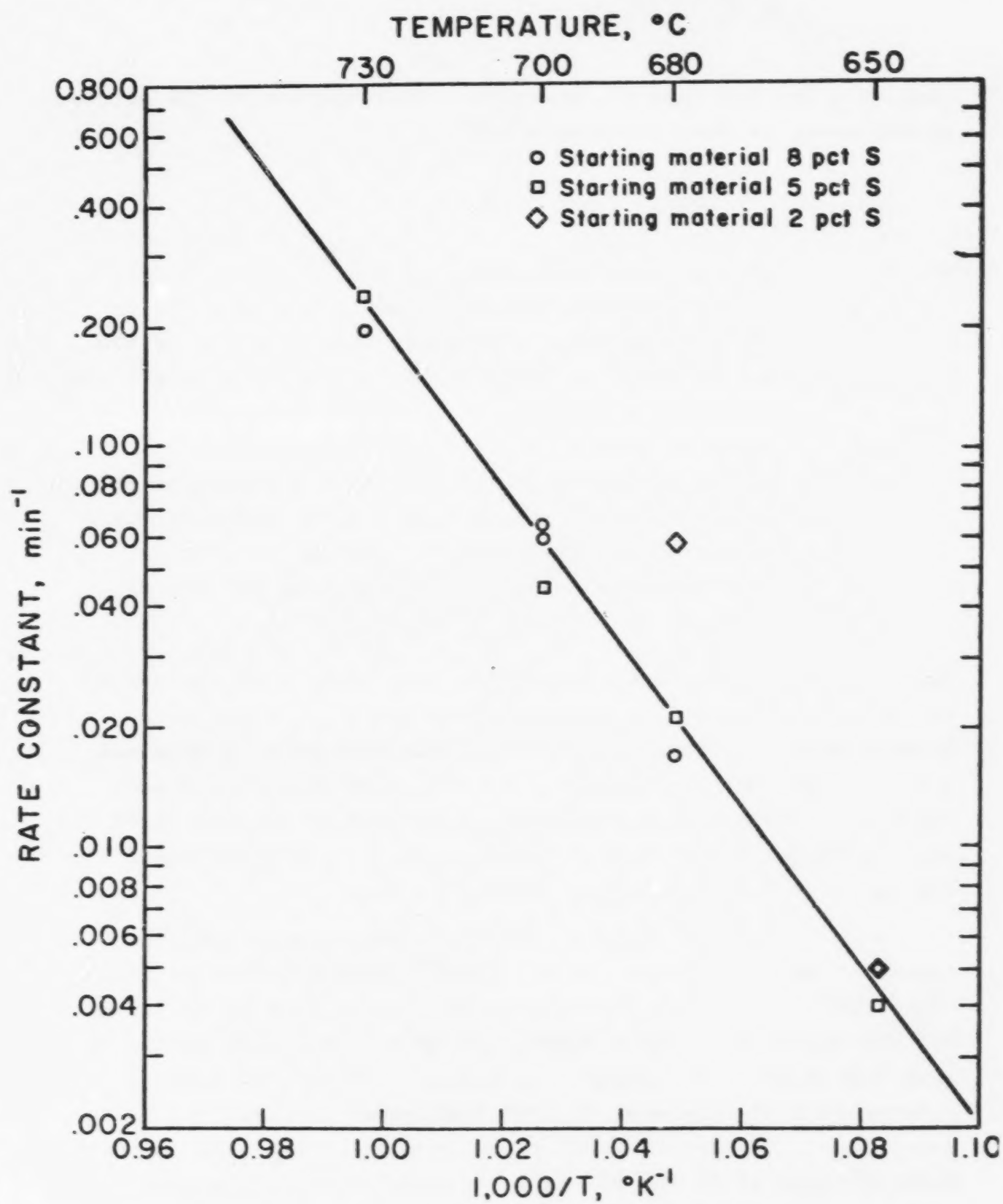


FIGURE 43 - Arrhenius Plot of Regeneration Rate Constants

69-39

time to a log function of the sulfur concentration on the sorbent as expressed in the following equation:

$$\log_{10} \left(\frac{W}{W_0} \right) = -Kt$$

where t = regeneration time (min.)

W = sulfur concentration on sorbent at time t lbs S/100 lbs sorbent. W excludes that fraction of the sulfur which occupies relatively inaccessible sites and neither participates in regeneration nor influences subsequent uptake.

W_0 = sulfur concentration (excluding the inactive fraction mentioned above) on the reactant at the start of regeneration (lbs S/100 lbs sorbent).

K = rate constant = f (temperature and sorbent properties) = 0.011 at 700°C.

Two different inlet sorbent loadings were used, 8.85 and 5.67% S, at 700°C and the results obtained from the Blyth model were plotted with the actual USBM-Albany regeneration data obtained for these sorbent loadings (Figure 44). The Albany data were taken from Table 1 of Albany Progress Report of January, 1969, and the interstitial sulfur loading used in the Blyth model was taken as 0.22% S based on the Albany data.

From Figure 44 it can be seen that the regeneration model satisfies the basic characteristics of the regeneration reaction, namely an initial high rate which levels off and approaches a zero reaction rate as the sulfur concentration approaches its interstitial value. However, the model gives a lower rate of regeneration than that which is predicted by the data, possibly due to the different sorbents used. The empirically derived value of K used in the Blyth model varies depending on the grade of sorbent used, and the CEGS data were obtained using an early grade Peter Spence sorbent whereas the Albany data are based on Grace No. 1 sorbent.

FIGURE 44

COMPARISON OF THE BLYTH REGENERATION MODEL

WITH

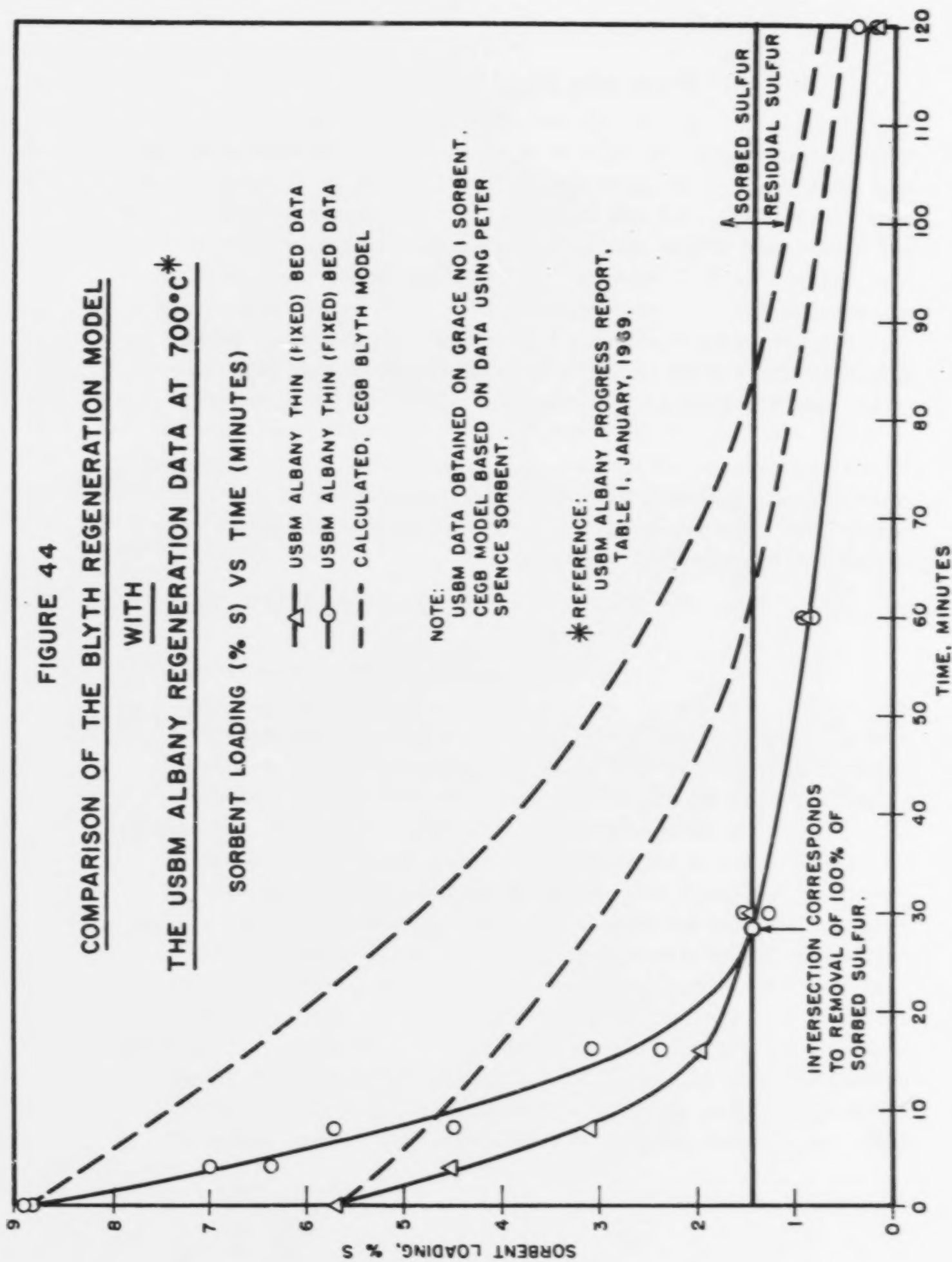
THE USBM ALBANY REGENERATION DATA AT 700°C*

SORBENT LOADING (% S) VS TIME (MINUTES)

- △— USBM ALBANY THIN (FIXED) BED DATA
- USBM ALBANY THIN (FIXED) BED DATA
- CALCULATED, CEGB BLYTH MODEL

NOTE:
USBM DATA OBTAINED ON GRACE NO 1 SORBENT.
CEGB MODEL BASED ON DATA USING PETER
SPENCE SORBENT.

*REFERENCE:
USBM ALBANY PROGRESS REPORT,
TABLE I, JANUARY, 1969.



(e) Evaluation of Various Sorbents

In the process of evaluating new SO_2 sorbents, differences in gas consumption rate during the regeneration reaction were found. In tests carried out at 1000 hr^{-1} space velocity (Table F-72), it was demonstrated that sorbents without iron had slow rates of gas consumption, low weight losses, and therefore, little sulfur removal. On the other hand, iron-containing sorbents showed fast consumption rates, high weight losses and more complete sulfur removal. High reaction rates may be responsible for a loss in hardness and resultant high attrition rates. Rapid chemical changes could alter the large crystallites by not allowing sufficient time for proper reorientation of the crystalline structure. The regeneration of the sorbents without iron is slower but the overall smoothness of the reaction might cause less strain on the pellets and possibly could result in smaller decreases in hardness.

1 - Kaiser DN-112-F, Kaiser B, Kaiser DN-105,
Peter Spence

Figure 45 illustrates the differences in the consumption rate of H_2 for two Kaiser alkalized aluminas with and without iron present, DN-112-F and B. The sorbent containing iron, DN-112-F, reacted rapidly with H_2 and was apparently reduced completely within 45 minutes as indicated by little or no additional H_2 consumption. Kaiser B, containing no iron, had a slow rate of gas consumption and was still consuming H_2 slowly even after 60 minutes. The other samples without iron, Kaiser DN-105 and Peter Spence produced H_2 curves similar to the Kaiser B sample. The data of Appendix Table F-72 show the sulfur removal obtained in the tests but do not indicate the base level sulfur concentration; i.e., the point at which all the sorbed sulfur is removed. Similarly, Figure 45 indicates point values of H_2 consumption up to over 70%, but the overall reducing gas utilization would probably be less than 70%, or some integrated average of this curve, depending

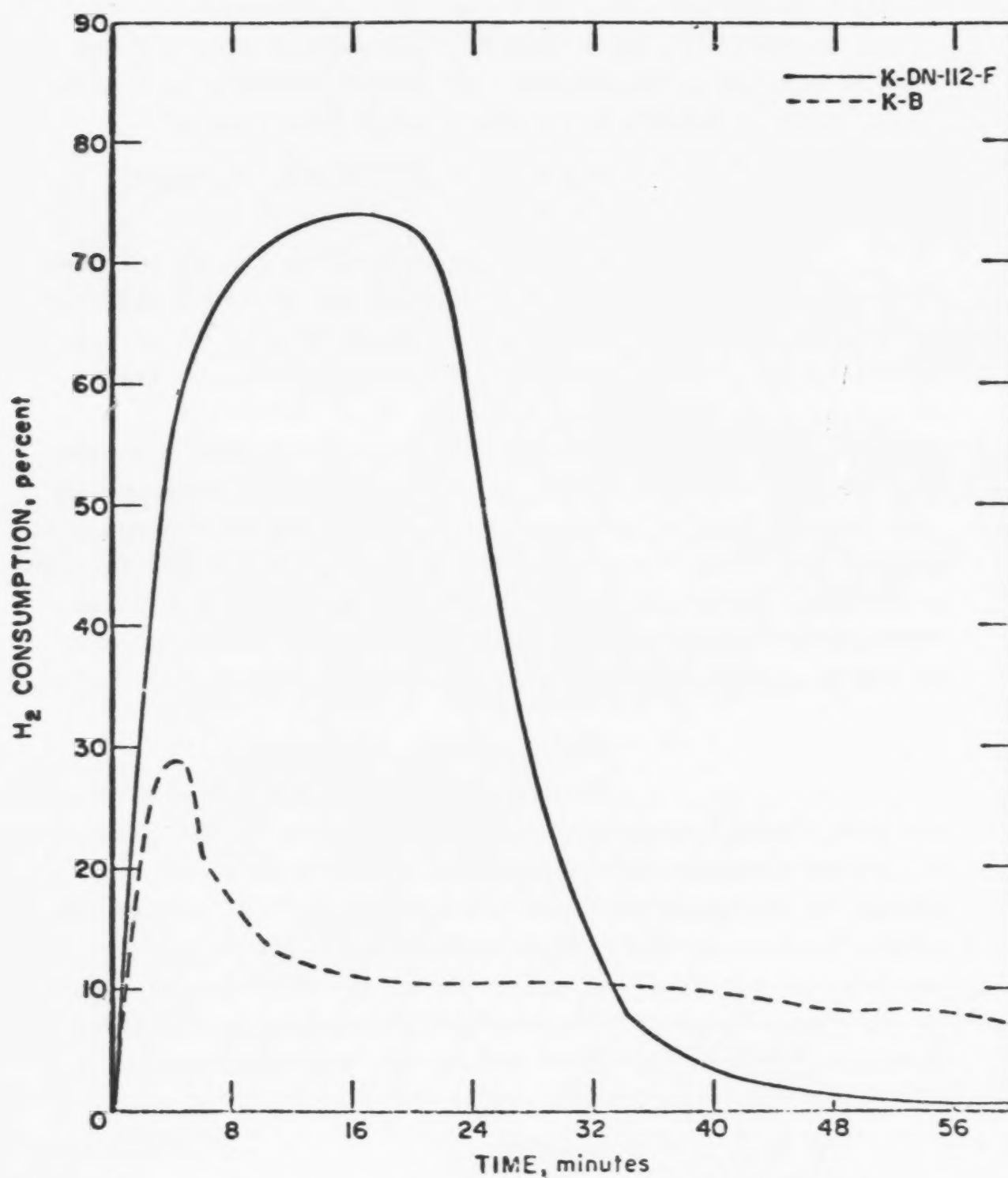


FIGURE 45 - Differences in the H₂ utilization at 660°C and 1000 hr⁻¹ space velocity of Kaiser DN-112-F containing iron and Kaiser (B) without iron.

on the time required to remove the sorbed sulfur. For the curve of Kaiser DN-112-F of Figure 45, in determining the actual degree of H_2 utilization, that portion of the curve from 32 minutes to 60 minutes would be considered as wasted, since the H_2 consumption is very small, less than 10%.

2 - Grace No. 2, Kaiser PR-15, Kaiser DN-113-F

Figure F-85 represents the H_2 utilization of iron-containing alkalized aluminas at 660°C and 1000 hr^{-1} space velocity. There was a slight difference in the H_2 consumption curve of Kaiser DN-113-F (similar to Kaiser DN-112-F) when compared with Kaiser PR-15 and Grace No. 2 materials at 660°C. The DN-113-F seems to be more reactive than the PR-15 and Grace No. 2 sorbents; its H_2 consumption goes rapidly to a single maximum and then the rate drops off, whereas the other two sorbents show two maxima before the rate falls off. At 680°C, the rate of consumption of all three sorbents showed curves similar to the Kaiser DN-113-F curve at 660°C, with a little higher maximum utilization of H_2 .

3 - USBM 423-X-4E, USBMX-3-F

The Bureau preparations of X-3-F and 423-X-4E reacted with H_2 in a manner similar to the other alkalized aluminas containing iron. Figure F-86 shows a family of curves of 423-X-4E regenerated with H_2 at various temperatures. At the highest temperature, 660°C, the gas consumption is rapid and the reaction is completed in about 30 minutes. The Bureau's X-3-F is a little more reactive than the 423-X-4E and there was an 82% sulfur removal at 660°C vs. 66% for 423-X-4E (Table F-72).

4 - Grace No. 1

Figure F-87 is a plot of the regeneration curves for experiments with the Grace No. 1 sorbent

(H-1-5-74-A) spent in the pilot plant. The use of 1:1 H₂:CO mixtures increased the utilization of reducing gas when compared to pure H₂ at 640- and 660°C. The types of curves produced are apparently a function of both the gas composition and temperature. Grace No. 1 alkalized alumina reduced with H₂ and CO mixtures indicated as much if not more sulfur removal than when pure H₂ was used. The opposite effect was found for the Kaiser PR-15 as shown in Table F-72. When it was regenerated with H₂ and CO mixtures at 660 and 680°C, there was less sulfur removed than when the reducing gas was pure H₂ at these temperatures.

5 - Two-Step Regeneration Reactions with Sorbents 1-4

The use of CO₂ as a secondary treatment after the primary reduction reaction seems promising. Table F-73 demonstrates the effect of using a secondary treatment with CO₂, mixtures of CO₂ and water vapor, and mixtures of N₂ and water vapor, after primary reduction reactions with H₂, CO, and their mixtures. The first series of tests using Kaiser DN-113-F and Kaiser DN-112-F indicates the effect of temperature during the secondary reaction with CO₂. To date, the best temperature found for the CO₂ treatment has been 300°C, when compared with the results at 600 and 100°C. A CO₂ treatment at 300°C almost doubled the sulfur removal obtained when using CO₂ at 600°C. The CO₂ treatment at 100°C was ineffective in removing any appreciable amount of sulfur from the Kaiser DN-112-F sample, only 25 percent total sulfur removal being achieved.

The addition of water vapor to the CO₂ gas improved the overall sulfur removal over the dry CO₂ treatment, but the presence of water vapor in N₂ (3 percent level) was not efficient.

The two-step regenerations carried out on the Peter Spence material showed poor sulfur removal properties. However, this poor response could be accounted for since the primary reduction reaction with CO was incomplete during the one hour reaction time.

The remainder of Table F-73 indicates the improvement in sulfur removal using CO₂ as secondary treatment for various sorbents. The Bureau's X-3-F showed sulfur removals as high as 86 percent when using a 1:1 H₂:CO primary reducing gas at 640°C followed by CO₂ at 325°C for a half hour.

6 - Bureau Prepared NaOH and Alumina Hydrate Sorbents

These sorbents were prepared with and without iron and their sodium content ranged from 11 to 22 percent. Preparations containing iron and those without iron showed reaction rates similar to alkalized aluminas tested previously. Table F-74 shows the results of regeneration tests and crushing strength changes of sorbents prepared with NaOH and alumina hydrate. Preparation No. 467 (1 percent iron as red mud) showed 85 percent H₂ utilization at the maximum consumption rate as compared to only 15 percent H₂ utilization for No. 466 having essentially the same composition except that there was no iron present. A comparison between preparations No. 470 (1 percent iron as Fe₂O₃) and No. 472 (no iron), shows similar results.

The sodium content of these sorbents also affected the reducing gas consumption rate. The lower sodium content preparations have a lower capacity to react with SO₂ but the material was harder and the regeneration reaction gave a higher maximum rate than with the high sodium sorbents. Sorbents Nos. 473, 474, 467 are similar in composition except for the amount of sodium present. No. 473 (11

percent Na) had the highest maximum rate of consumption but had the lowest sulfur loading. No. 474 (17 percent Na) showed a maximum reaction rate between No. 473 and No. 467 (22 percent Na). The hardness dropped 50 percent for sorbent No. 467 (highest Na) but only 21 and 24 percent for No. 473 and No. 474, after the H_2 regeneration at $660^\circ C$. The sorbents without iron showed little reaction and their hardness was retained.

Two step regeneration using CO and then CO_2 on sorbent No. 473 indicated similar results to those obtained previously, namely that a secondary CO_2 treatment at $300^\circ C$ increases the sulfur removal.

7 - UOP Alumina Pellets Impregnated with Active Compounds

The sorbent formed by sodium aluminate and ferric nitrate impregnated on alumina retained its high hardness after H_2 regeneration, but the regeneration was incomplete (sulfur removal only 60 percent - Table F-74). Figure F-88 illustrates the similarity of the two rate curves for $640^\circ C$ and $680^\circ C$, and shows both regenerations to be completed within 30 minutes even though the sulfur removal was not more than 60 percent. The regeneration with H_2 was very fast and the reaction did not show the temperature dependency demonstrated by the alkalized aluminas. The UOP-V-1 sorbent (Na_2SO_4 and $Fe_2(SO_4)_3$ impregnated on alumina) showed softness even before the regeneration reaction, apparently due to some interaction between the alumina carrier and the sulfate.

8 - Kaiser PR-18-1 Alkalized Alumina (15% Na and 0.6% Fe)

This alkalized alumina reacts in a manner similar to the other alkalized aluminas but the H_2 regeneration curves at 680° and $660^\circ C$ tend to flatten out at the maxima, rather than reaching a high peak and then falling off rapidly. This flat-topping may indicate a rapid but controlled diffusion.

The change in maximum consumption rate of the reducing gas at 640°C reaction temperature is illustrated in Figure F-90. The higher the CO content of the reducing gas, the greater the maximum consumption rate. Table F-74 indicates that the regenerated pellets have low hardness values but they are better than Grace alkalized aluminas (Table F-75).

9 - Grace No. 1 and Grace No. 2 Comparison

Table F-75 compares the regeneration of totally spent Grace No. 1 and Grace No. 2. The two-step regeneration with CO at 680°C followed by CO₂ from 680°C to room temperature was not effective in either case. Both Grace alkalized aluminas when spent to SO₂ saturation show similar regeneration data at the same reaction temperature. At 700°C the reaction rates are not much different than at 680°C, other conditions being the same. A red deposit of residual sulfide was found on the pellets even at 700°C where the sulfur removal was over 80 percent. Regeneration at 640°C took two hours to complete at the 1000 hr⁻¹ space velocity with a maximum utilization of about 40 percent of the hydrogen. The hardness of the Grace alkalized aluminas could not be restored to their original "raw material" value once the regeneration or activation reaction took place. The Grace No. 1 sorbent was always harder than Grace No. 2 after similar treatments.

(2) AVCO Studies

Avco collected data on 250 mg. differential bed samples. Generally the few data reported were scattered, but the following trends were observed:

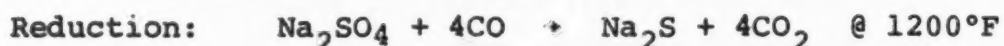
- Regeneration time decreased as the partial pressure of H₂ increased for sorbent loadings of 3.6 + 5.5 weight percent SO₂ (Table F-76). On the other hand, CEGB reports (June 1965) that the rate was independent

of hydrogen pressure above 70 mm Hg.

- Regeneration time increased rapidly with increased initial sorbent loading. For a fixed loading, regeneration time decreased rapidly with increasing temperature (Table F-77 and Figure F-91).
- In the presence of pure CO, the reaction does not go to completion; i.e., after constant weight is reached in the H₂-CO mixture, exposure to pure H₂ will produce further weight loss (Table F-78). As much as 25% of the sorbate is unremoved.
- In the presence of the reaction products, H₂S and H₂O, the regeneration rate was not significantly lowered but ceased at 75% completion and pure H₂ was required to complete the process. CEGB reports (June 1965) that rates measured at 654°C for a constant H₂S pressure were found to be independent of H₂S partial pressure but considerably lower than those determined in the absence of H₂S.
- It appears that thermal regeneration decreases as sorption time increases. At a given sorption time, there seems to be no effect of flue gas SO₂ concentration (Table F-79).
- The effect of the humidity of the flue gas and initial sorbent loading on the temperature dependence of regeneration time was not measured. Few data were taken and the temperature effect from 550-650°C was obtained on sorbents of low initial loading on which the SO₂ was sorbed from dry flue gas whereas the temperature effect from 650-700°C was obtained on sorbents with a high loading, loaded in moist flue gas (Table F-80).

(3) W. R. Grace & Company Studies

A two-step regeneration procedure, consisting of a high temperature reduction step with a reducing agent such as CO and a low temperature hydrolysis step with water and CO₂ to complete the regeneration, is undergoing evaluation presently. The theoretical equations proposed are:



@ >212°F

The reduction rate of Na₂SO₄ by CO is highly temperature sensitive. Grace No. 2 beads loaded to approximately 5% S were reduced at three temperatures under two CO flow rates (Table F-81), and substantial exotherms, 104 to 160°F, were observed in all cases. Table F-81 also indicates that regeneration of the reduced Na₂SO₄ is accomplished more rapidly with a CO₂ - H₂O blend than with a N₂ - H₂O blend. Two temperatures, 340°F and 500°F, and three CO₂ to H₂O ratios were examined. Fastest rates were achieved with a 3/1 CO₂ to H₂O ratio at a temperature of 340°F. Exotherms varied from 60 to 100°F, with the largest occurring under the above conditions. Accordingly, a two-step regeneration reaction shows promise in the reduction of the regeneration time. Also, if CO and CO₂ are used for regeneration, the formation of steam during the reduction process would be eliminated. Therefore, the amount of water vapor that contacts the sorbent during regeneration would be reduced. In order to eliminate steaming effects at high temperatures when hydrogen is used as the reducing gas, reformed natural gas is preferable to producer gas since the CO content is higher and the H₂ content lower.

c. Summary of Status of Data

The exact mechanism by which the sorbent is regenerated has not been defined clearly but sufficient data are available to permit a preliminary design of a regenerator to be made. To allow for the uncertainties in the regeneration step, safety factors have been included in the regenerator design but actually cause only modest increases in the vessel cost.

The general conclusions that can be drawn from the regeneration data available are:

- Increasing the temperature increases the regeneration rate and temperatures about 1300°F or higher appear to be indicated to obtain a reasonable hold-up time in the regenerator.
- Pure H₂ or mixtures of H₂ and CO (i.e., reformed natural gas) give satisfactory regeneration but pure CO does not. Natural gas itself does not give complete reduction. Other reduction methods (e.g. two-step using CO, CO₂-H₂O) are being evaluated but no firm conclusions can be drawn at this time.
- If the sorbent does not contain a small amount of iron (1%) then commercially unacceptable regeneration rates are obtained.
- The effect of repeated sorption-regeneration cycles on sulfur build-up in the sorbent has not been determined. That is, the life of the sorbent owing to loss of activity (sorption capacity) rather than to attrition is presently unknown.
- There are some indications of sulfide formation but its effect on the process has not been determined; possible effects might be stripping of SO₂ in the sorber or higher reducing gas consumption.
- Some data have been obtained which indicate little, if any, effect of H₂S back pressure on the rate or degree of regeneration. This is important since backmixing of the gas is likely in a fluid bed regenerator.

B. PRELIMINARY PROCESS DESIGN

1. Pilot Plant Studies

At the request of NAPCA, a quick process design and approximate cost estimate for several different demonstration-scale alkalized alumina (AA) processes were prepared. Each of the AA plants is sized to remove 90% of the sulfur from the flue gas generated by a 50 megawatt (MW) power plant. The two basic designs differ primarily in reactor design; one case considers the use of a dispersed phase reactor similar to the one in the USBM-Bruceton pilot plant, while the other utilizes a fluid bed reactor.

Originally, the fluid-bed reactor was to have three beds in series and the flue gas sulfur oxide content was that used by the Central Electricity Research Laboratory (CERL) in their fluid bed work. This sulfur concentration corresponded to a flue gas obtained by burning a coal containing about 7% sulfur. Further, the flue gas temperature was specified as 264°F, thus requiring a flue gas preheater for evaluating sorption temperatures higher than this. Regeneration conditions were also based on CERL data.

The CERL regeneration rate correlation shows a relatively slow rate at 650°C (1202°F) compared to that at 700°C (1292°F) (e.g., about 25% sulfur removal after two hours vs. about 95%), so to avoid excessive hold-up in the regenerator, the higher temperature was used for the regeneration step in the fluid-bed design.

The dispersed phase design was to be based on flue gases obtained from burning a 3% S coal, with these gases available at 600°F. Regeneration conditions were based on Bruceton pilot plant practice, namely, a regeneration temperature of 1200°F and a four hour holdup. Preliminary process designs and cost estimates were prepared for these original cases. It was

subsequently decided to extend the study and prepare a design and estimate for each scheme (i.e., fluid-bed and dispersed phase) that could be directly compared. Therefore, to provide a case for direct comparison, a 700°C regeneration temperature was also used in a dispersed phase case design. It was further decided to use only one bed in the fluid bed reactor since calculations showed that three beds were not required to achieve the desired sulfur removal.

Flow sheets for the demonstration-scale unit are basically the same as those developed for the base case design (1000 MW power plant), which are discussed in other sections of this report. (For 50 MW flow sheets, see MWK Progress Report #8).

The factors common to all estimates are (a) 90% removal of the sulfur oxides from the entering flue gases, (b) natural gas to generate reducing gases for sorbent regeneration; and (c) a Claus plant to convert hydrogen sulfide to sulfur. It should be pointed out that approximate estimating techniques have been used in developing the estimates. The experimental data are incomplete and the process designs were not optimized so more precise estimating procedures did not seem justified at the time. The battery limits estimates, and the total capital requirements of the erected plants (including offsites and sorbent inventory) for the basic flow sheets, along with the alternatives, are given in Table 30.

Referring to the dispersed phase cases, it is obvious from the tabulated plant costs that for these designs flexibility in sorption temperature is costly, i.e., DP-2 costs about \$600,000 more than DP-1. It is also apparent that an increase in regeneration temperature from 1200°F to 1292°F causes a significant increase in plant cost: about \$500,000, comparing cases DP-2 and DP-3. This latter increase is due primarily to more costly vessels required arising from the decrease in allowable metal stress at the higher temperature.

TABLE 30

BATTERY LIMITS ESTIMATES AND TOTAL CAPITAL REQUIREMENTS* (50 MW PLANT)

	COST, THOUSAND DOLLARS	
	BATTERY LIMITS	TOTAL
<u>Dispersed Phase (3% S in coal)</u>		
1. Base Case: 600°F sorption 1200°F regeneration-4 hrs	4,000	4,905
2. 264-655°F sorption 1200°F regeneration-4 hrs	4,535	5,515
3. 264-655°F sorption 1292°F regeneration-2 hrs	5,030	6,080
<u>Fluid Bed</u> (includes electrostatic precipitator)		
1. Base Case: 3 beds, 7% S in coal 264-655°F sorption 1929°F regeneration-2 hrs	7,560	8,695
2. 1 bed, 3% S in coal 264-655°F sorption 1292°F regeneration-2 hrs	5,735	6,895

* Includes offsites and sorbent inventory

Although the vessel design has not been optimized, a brief look at various alternatives (e.g., brick lined) showed no obvious substantial savings to be realized from different types of design. Therefore, the conclusion that the higher regeneration temperature causes a substantial cost increase may still be valid for optimized designs.

The investments for the two fluid bed cases show that a substantial decrease (\$1,800,000) is obtained by designing for one fluid bed (rather than 3) and 3% sulfur in the coal. The investment required for a fluid bed plant is about 13% higher (-\$800,000) than required for a dispersed phase plant when the two are compared on a common basis, i.e., DP-3 and FB-2.

Considering the approximate nature of the estimates, the difference in the plant investment required by the two different comparable designs (DP-3 and FB-2) is too small to indicate a clear superiority of one system over the other.

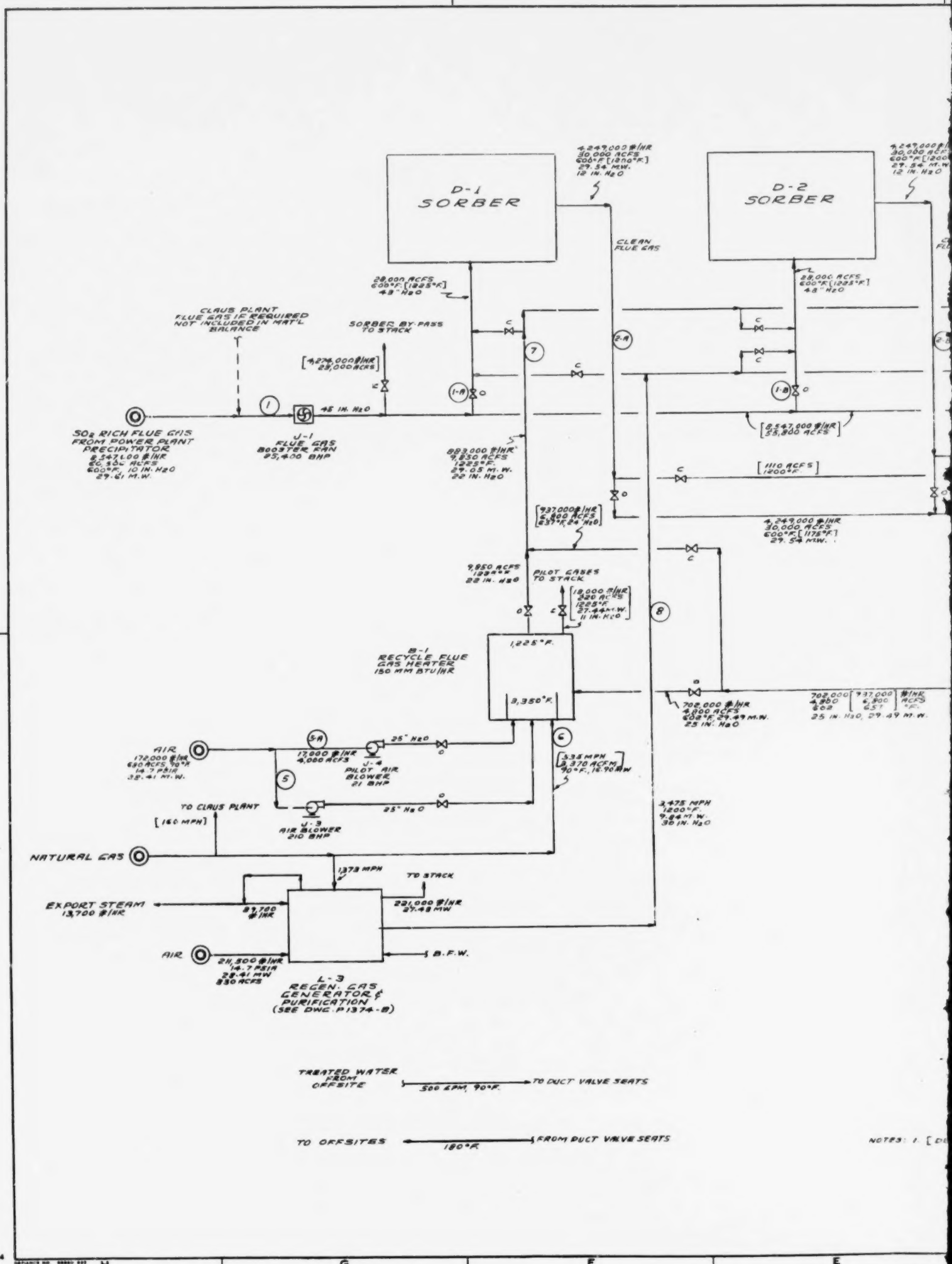
The purpose of preparing these 50 MW plant designs was to determine the approximate cost of building and operating a pilot plant which at one time the Central Electricity Generating Board (CEGB) was considering. CEGB was looking for partners to share the expense of such a plant and NAPCA wanted an independent estimate of the cost in case they decided to join CEGB in the venture. The project was later abandoned, presumably owing to their lack of success in developing a commercially acceptable sorbent.

2. Commercial Scale Studies

a. Dispersed Phase

(1) Dispersed Phase Process Description: Flow Sheet P3197-D

The following process description is for the Alkalized Alumina process scheme shown on flow sheet P 3197-D.



A

B

The scheme is based on removing 90% of the SO_2 in the flue gases from a 1000 MW power plant burning coal containing 3% sulfur. It should be noted that the quantities shown are for only one train of equipment whereas two parallel trains are required when the power plant is running at full capacity.

Hot flue gases (about 600°F) from the power plant enter the bottom of the dispersed phase reactor, D-1, and flow upward through the reactor at about 25 feet per second with a total gas residence time of about three seconds being achieved. In the reactor the flue gases contact the sorbent particles under conditions designed to effect removal of 90% of the SO_2 present in the entering flue gas. The treated flue gas effluent from the top of the reactor passes through a one-stage cyclone to recover sorbent particles greater than about 60 mesh, and then it sent to the power plant stack after first flowing through the air preheater and electrostatic precipitator. An alternative design would relocate the electrostatic precipitator upstream of the SO_2 removal plant. The air preheater and electrostatic precipitator are standard pieces of equipment in power plant operations and are not part of the SO_2 removal process.

Sorbent is introduced into the D-1 reactor at three different points: a heavy particle recycle stream near the top of the reactor, a fines recycle stream which enters near the bottom of the reactor, and a stream of regenerated sorbent also near the bottom. The heavy particle stream comprises particles whose settling velocity is greater than the superficial gas velocity in the reactor, and thus these particles fall downward through the reactor and are withdrawn from the bottom. The regenerated solids consist of a range of particle sizes, including particles with settling velocities both greater and less than the reactor gas velocity. The heavier particles settle to the bottom and are withdrawn through the bottom exit line while the lighter particles are carried

upward and are recovered in the reactor cyclones. The fines recycle stream is comprised of a portion of the fines recovered in the reactor cyclones.

The bottom exit solids are transported via a dense phase riser line to the top of the reactor where the fluidizing air and solids are separated in the gas-solids separator, L-2. The air leaving L-2 is combined with the flue gas leaving D-1 for eventual discharge to the atmosphere via the power plant stack. The solids in the bottom of L-2 are maintained in a fluidized state and are withdrawn through a standpipe and split into two streams: a recycle stream to D-1, and a side stream which is sent to the regeneration section.

The lighter sorbent particles carried overhead with the flue gas move through the reactor at different velocities depending on the slip velocity of the individual particles (i.e., slip velocity is the difference in gas velocity and particle settling velocity), and therefore have different residence times in the reactor. Thus the heavier of the overhead particles have the lowest slip and hence highest residence time. The lightest particles have the shortest residence time. However, these short residence time particles have a high surface area to weight ratio. Therefore, it has been assumed that most of these overhead particles will have either sufficient residence time or sufficient exposure of surface area such that they will be loaded to design capacity during one pass through the reactor and will not have to be recycled. In case one pass is not sufficient, however, provision for recycle of some of the fines back to the reactor has been included on the flowsheet.

Entrained fines in the flue gas effluent from the top of D-1 are recovered in cyclones L-1A-1F. The large volume of gases to be handled require the use of several cyclones in parallel. The flue gas effluent from these cyclones is sent

to the power plant stack, while the recovered fines (+60 mesh particles) may be recycled to the reactor or may be combined with the side stream of heavier particles from L-2 and sent to the regeneration section as discussed above.

The regeneration section comprises a solids heater, D-2 and a regenerator, D-3. These vessels are operated at a nominal pressure of 30 psia (selection of the operating pressure is discussed later), whereas the D-1 reactor pressure is essentially atmospheric. Thus, it is necessary to feed solids from a system at low pressure into one at high pressure and vice versa. The latter condition can be met easily by taking a suitable pressure drop across the solids feeder, but the former requires a build-up of pressure in the solids transfer line between the D-1 reactor and solids heater D-2. This has been done by use of a dense phase solids standpipe extending from the bottom of the elevated L-2 gas-solids separator to grade. The height of the standpipe is such that the pressure at grade is equivalent to that in the solids heater. Air is injected into the line at grade such that the solids are pneumatically transported to the solids heater and fed into the top bed through a feed nozzle designed to separate the air and solids so that bed stability is not affected. The transporting air mixes with the gases leaving the top bed, the combined gas stream then passes through an internal cyclone for fines removal, and finally joins the main flue gas exit stream. If a single bed heater were used, the solids from D-1 could be injected directly into the bed and the transporting air would then supply part of the combustion air thus reducing the air compressor horsepower. A two stage heater proved to be more economical, however, since the reduced fuel requirements more than offset the horsepower savings.

Sorbent solids are heated from 658°F to 1400°F in solids heater D-2, which contains two fluidized beds: (1) a top bed which preheats the cold solids by exchange with hot exit gases from the bottom bed, thereby effecting heat economy, and (2) a bottom fluidized bed in which the solids are heated to the desired temperature of 1400°F by direct combustion of natural gas in the bed itself. Hot solids leave the bottom bed through an overflow withdrawal line and are fed into the moving bed regenerator, D-3. A slide valve in the discharge line from D-2 and a splash baffle underneath the end of the line in D-3 provide a seal to prevent the spent regeneration gas from flowing into the D-2 solids heater.

Sorbent is regenerated in D-3 by countercurrent contact with upflowing regeneration gas. The regeneration gas is supplied to the regenerator from the steam-methane reformer, L-3. The reformer gas generation process flowsheet (Pl374-B) and description are given in Section B.2.e. part (1) of this report.

The sorbent which is loaded with sulfur in the form of SO_4 or SO_3 is converted back to its original state (NaAlO_2) by the reducing atmosphere in the regenerator. The 1400°F regenerator off-gas which contains the reduced sulfur in the form of H_2S exits from the top of the regenerator and after passing through the waste heat boiler, C-2, it is routed to the Claus Plant for the recovery of elemental sulfur. A description of the Claus Plant is given in section 6, part (3) of this report.

The regenerator is designed to provide (1) a bed which moves down through the vessel in a plug-type flow pattern, and (2) uniform gas distribution throughout the bed. These objectives are achieved by (1) installing suitable baffles near the vessel bottom, and (2) providing gas distribution

rings spaced so that equal bed heights are obtained above each ring by allowing for build-up of sorbent due to a single inlet line and the angle of repose of the sorbent.

Hot, regenerated sorbent is withdrawn through a standpipe and is pneumatically transported to the bottom of reactor D-1, thus completing the solids cycle. Make-up sorbent is stored in hopper F-2, and added to the system as required by feeding it in through the regenerated solids transfer line.

The air required for the solids heater D-2 and that needed for fluidizing and transporting purposes, is supplied by the centrifugal air compressor J-1. The J-1 discharge stream is split into four separate streams: the three streams used for transporting the solids and the stream to the solids heater.

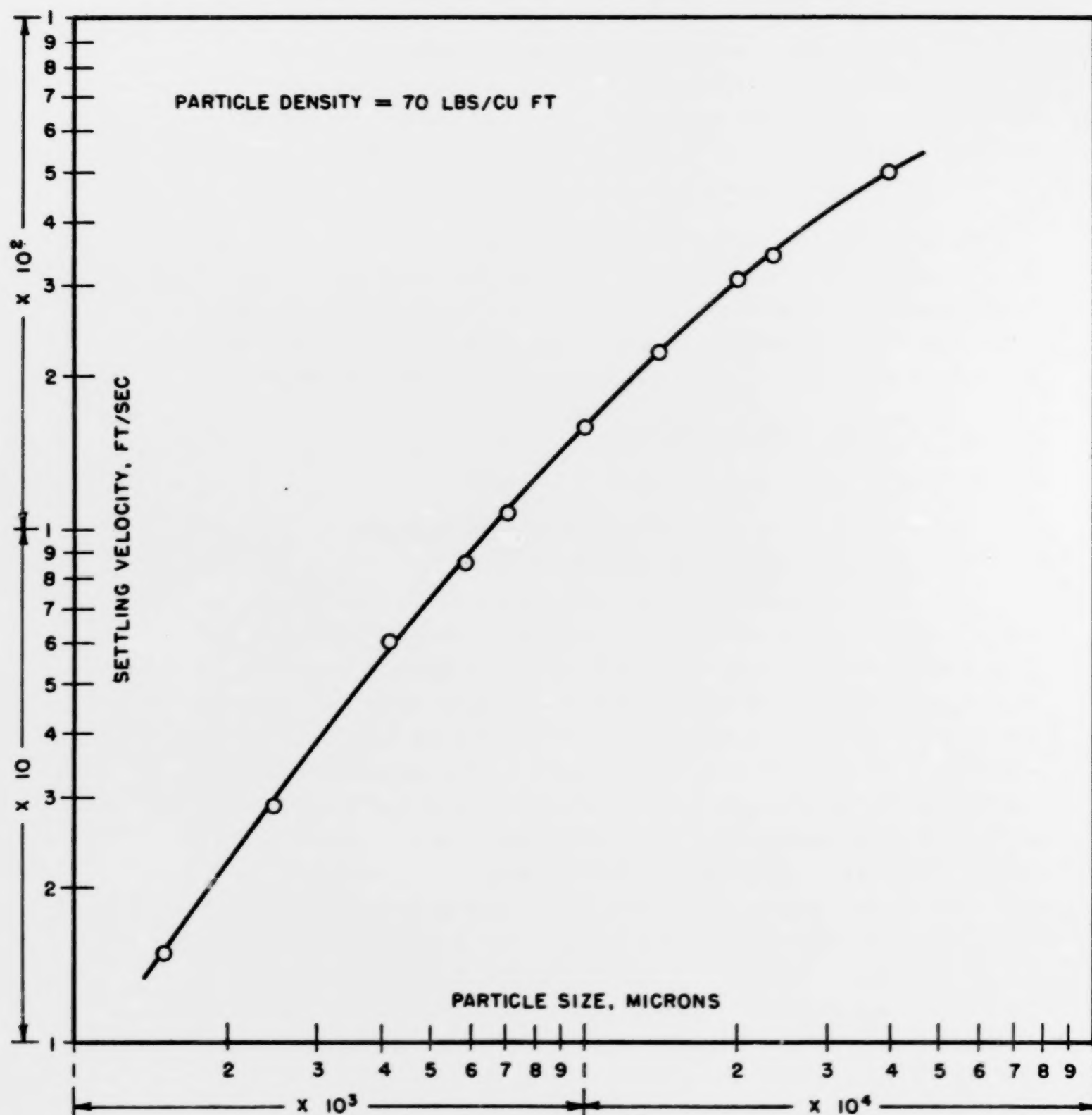
2. Design Notes - Dispersed Phase

a. Preliminary Calculations

(1) Effect of Gas Velocity and Recycle on Residence Time in Absorber

An attrition run reported in the Bruceton Quarterly for the period ending 12-31-67 contained a sorbent size distribution ranging from 246μ to 2362μ (60 to 8 mesh). This distribution was based on a composite of streams (bottoms, recycle, and overhead) from the absorber. Although this distribution is for a very friable sorbent it was used in the preliminary design because no other pertinent data were available and the distribution per se, in the range considered, does not greatly affect process design since both overhead and bottom recycle lines are provided. For each of the average particle sizes tabulated, theoretical settling velocities were calculated: based on physical properties of the system, a function of the Reynold's Number was calculated from which the Reynold's Number and hence the particle settling velocity could be calculated. Figure 46 is a plot of this cal-

FIGURE 46
SETTLING VELOCITY VS PARTICLE SIZE



culated settling velocity vs particle size. As can be seen from this plot, the settling velocity of the average (i.e., 50% size) particle size, 1050 microns, is approximately 16 ft/sec but the settling velocity of the different size fractions ranges from 33 ft/sec for the largest particles (2362 micron) down to 3 ft/sec for the smallest, (246 microns). This wide range of settling velocities results in large differences in residence time in the absorber for the different size particles. The preliminary process evaluation for a 1000 megawatt power plant will use a 25 ft/sec gas velocity in the absorber. However, a lower gas velocity may increase the solids residence time in the absorber and improve efficiency since the settling velocity calculations indicate that at 25 ft/sec gas velocity the heavier particles will fall rapidly through the absorber while the fines (-60 mesh, 240 microns) will be rapidly blown out, thereby not achieving maximum usage for sulfur removal. The lower velocity would, of course, require larger diameter reactors which would be more expensive.

Based on the feed cited above, the theoretical residence time for each size fraction has been calculated for superficial gas velocities in the absorber of 20 and 25 ft/sec. The weighted average solids residence time in the reactor was calculated from the weight fraction and residence time of each sorbent size. The results of these calculations are presented in Table 31 and show that for the conditions used, lowering the gas velocity from 25 to 20 ft/sec will increase solids theoretical weighted average residence time by about 16%. The longer residence time should provide increased sulfur pickup, other conditions remaining constant.

It should be noted that while the residence time of all particles greater than 10 mesh is decreased by the lower gas velocity, all the particles less than 10 mesh have longer residence times. By recycling the bottoms to the absorber

TABLE 31
CALCULATED SOLIDS RESIDENCE TIME IN BRUCETON REACTOR

TYLER MESH	AVG. SIZE, MICRONS	WEIGHT FRACTION	V_s THEOR. SETTLING VELOCITY FT/SEC	$V_g - V_s$, FT/SEC.		RESIDENCE TIME, * SECONDS				(WT. FRACT.) x (RESIDENCE TIME)	
				25 [†]	20 [†]	OVERHEAD	25 [†]	20 [†]	BOTTOMS	25 [†]	20 [†]
+8	2362	0.0074	33	-8	-13	—	—	—	5.00	3.08	0.04
-8 +10	2006	0.2127	31	-6	-11	—	—	—	6.67	3.63	1.42
-10 +14	1410	0.2403	22	+3	-2	18.35	—	—	20.	—	4.41
-14 +20	1000	0.1373	16	+9	+4	6.11	13.75	—	—	—	0.84
-20 +28	711	0.1055	11	+14	+9	3.93	6.11	—	—	—	0.42
-28 +60	418	0.2171	6	+19	+14	2.89	3.93	—	—	—	0.63
-60	<246	0.0797	3	+22	+17	2.50	3.24	—	—	—	0.20
Weighted Average Residence Time										7.96	9.24

*Note: Residence time is based on the overhead stream particles being fed into the absorber at the 20 ft. level and dropping another 10 ft. so that they travel a total distance of 55 ft. The bottoms particles are assumed to be fed into the reactor at the 40 ft. level and thus travel only 40 ft. total.

† Gas velocity in ft/sec, V_g

(instead of once through operation as is now used), the residence time of the larger particles could be increased. This has been discussed with the Bruceton people and a bottom recycle line was eventually installed but operation of the pilot plant was stopped before data could be obtained using this new recycle line on particles having a substantial size distribution. Some mechanical performance data were obtained using a catalyst support material (UOP alumina spheres) of uniform size but the results were inconclusive since only a few runs were made.

The H-series data (Table 17) show that runs H-106-H-111 and H-115-H-119, or a total of 11 out of 15 runs, indicate lower sulfur concentrations in the reactor bottoms than in the fresh sorbent feed. These data seem to substantiate the theory that under the present method of operation, the heavier particles remove very little sulfur from the flue gas and thus a large portion of the fresh sorbent feed is essentially inactive. The feed comprises a range of particle sizes with different sulfur content but only the average is reported. However, the heavier particles fall out the bottom and if their sulfur content initially is lower than the feed average, and if they pick up very little sulfur in the reactor, the sulfur content of the exit stream could be lower than that in the fresh feed. This would explain the H-series results cited above where the bottoms exit sulfur concentration is lower than the fresh feed. To better define the amount of sulfur pickup as a function of particle size, it would seem worthwhile to separate (screen) the different streams (i.e., feed, recycle, bottoms, sorber) into several size fractions and analyze for sulfur in each reaction. This procedure would furnish data to either confirm or disprove the theory that the bottoms fraction contributes very little to sulfur removal.

(2) Effect of Sorbent Density on Sulfur Removal

The USBM Section I Quarterly Report of 6-30-68 states that a venturi throat was installed near the sorber bottom and as a result the solids residence time was increased. It also states that in tests using a sorbent density of 0.30 lbs/ft³ in the absorber nearly all of the SO₂ was removed from the flue gas. However, the only sorption data included are for the H-series which are tabulated in Table 1 of the USBM report and the maximum sulfur oxides removal shown in 68.4%. Apparently, the venturi was not used in the H-series but no data are included to support either the value of 0.3 lbs/ft³ solids density or removal of nearly all of the sulfur oxides.

In previously reported data on hand, only a relatively few runs have actually shown 90% sulfur oxides removal; i.e., the only runs showing at least 88% SO₂ removal are E-101, E-107, E-109, F-103, F-104, F-107 (See Table 16). Because all process designs are based on 90% SO₂ removal, it would seem desirable that a steady state pilot plant run of appreciable duration (say 1-3 days) should be made to demonstrate that 90% removal is practical under commercial conditions. This run could, of course, be combined with a run designed to measure sorbent attrition losses when improved sorbents become available.

Since density in the sorber is an important variable in degree of sulfur removal from the flue gas, the H-series runs were used to determine the correlation between pressure drop and density. The absorber pressure drop measurement is direct whereas the density is determined by simultaneously stopping the flue gas, fresh solids feed, and recycle solids flows. The sorbent in the reactor column is then collected and weighed and the density calculated based on column volume and sorbent weight. It is felt the pressure drop measurement

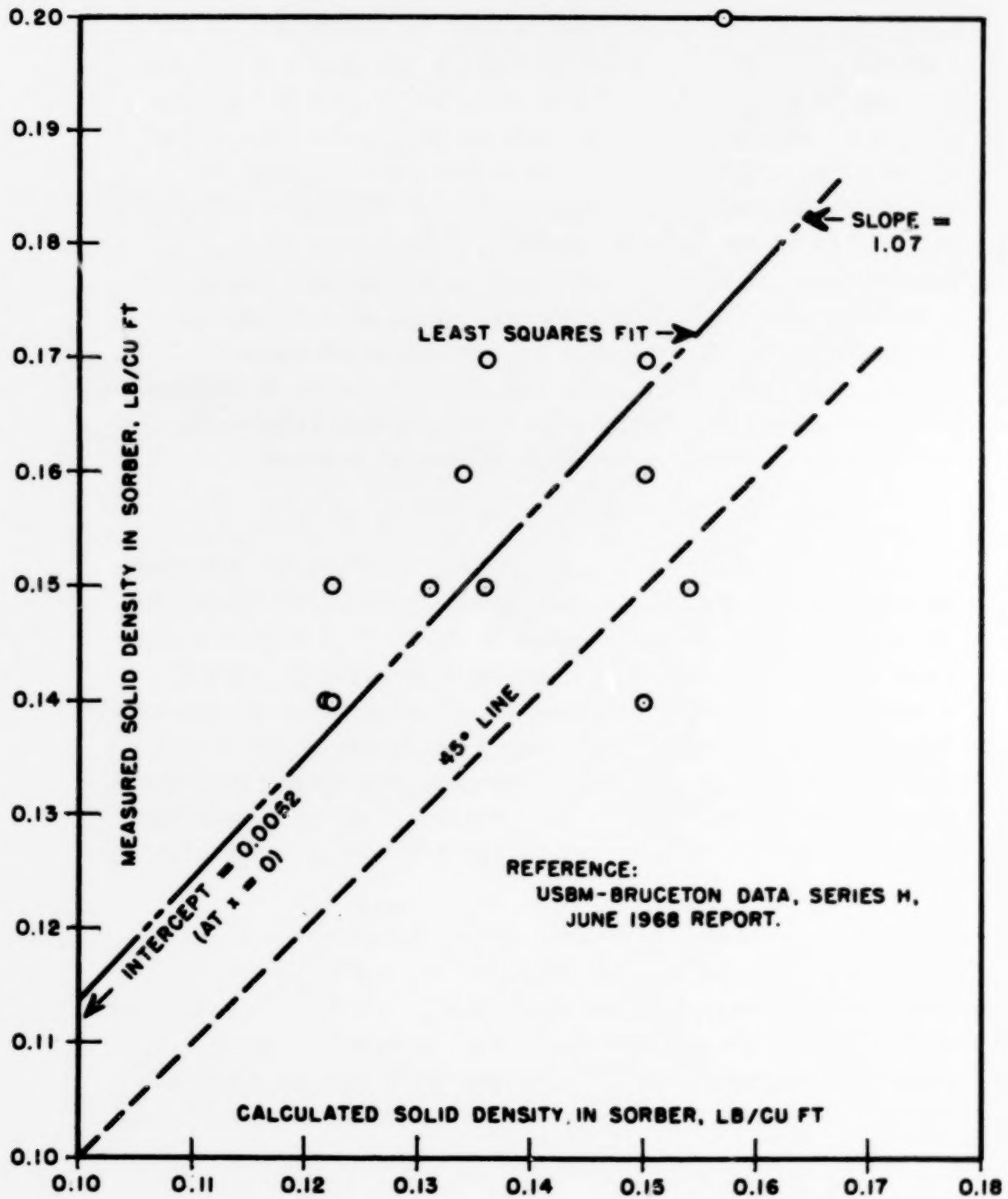
is the more accurate and consequently it has been used to calculate the sorber density. These calculated values have been plotted against measured values in Figure 47. A 45° line through the origin shows most of the measured points are higher than the calculated points. A possible reason for this could be that there are solids in the feed lines downstream of the shut-off valves and these solids, which do not contribute to pressure drop, are collected along with the solids in the sorber itself. A least squares fit for all of the data points from tests using recycle solids has been made and a line obtained with slope of 1.07 and an intercept of 0.006, compared to a theoretical slope of 1.0 and an intercept of 0. Thus the correlation is considered good enough to justify the use of calculated values for either density or pressure drop in design studies.

(3) Regenerator

The preliminary process calculations for the moving bed regenerator are summarized below. It should be noted that the discussion below is based on a regeneration temperature of 1200°F which was later changed to 1400°F. However, the following discussion which is based on the 1200°F regeneration is valid except for a few minor points for a 1400°F operation and therefore has been included even though it does not represent the final design. The rationale for switching to 1400°F is given in the section on vessel design-solids heater.

Reformed natural gas, consisting of 76.9% H₂, 13.1% CO₂, and 10% CO, was selected for the regeneration of alkalized alumina, with an arbitrarily specified utilization of 80% (i.e., 25% excess) for design purposes. Since very little experimental data on product distribution (both gas and solid phases) were available at the time of this design,

FIGURE 47
SORBER DENSITY
CALCULATED VS MEASURED



it was decided that product distribution based on thermodynamic calculations was a reasonable choice for a design basis. Further, since these calculations already had been done by AVCO it was decided to use their results, modified as required by slightly different conditions. As a check on AVCO's values, a product distribution was calculated using an internal Kellogg computer program and for the conditions selected, the results were generally in good agreement. The AVCO 16th Monthly Summary, April 29, 1968, Table VIII, p. 50 lists the product distribution at chemical equilibrium for alkalized alumina with the above reformed natural gas composition for a temperature range of 527-927°C (980-1700°F) at 100°C intervals, and a sorbent molecular formula of $1 \text{ Na}_2\text{O} + 2.435 \text{ Al}_2\text{O}_3$, which is equivalent to 20 weight percent (wt %) Na_2O . The solid phase consists of NaAlO_2 and excess Al_2O_3 , with a residual content of Na_2SO_4 for temperatures below 727°C. The gas phase is primarily H_2O , CO_2 , and H_2S , but above 700°C, S_2 , SO_2 , and COS concentrations increase. For the present MWK case, the inlet solids feed to the regenerator contains 3 wt % S and is to be regenerated at 1200°F and 15 psig, to a residual level of 0.5 wt % S whereas AVCO's regenerated product at 627°C (1161°F) contains 0.45 wt % S. The difference in sulfur content is probably too small to have a significant effect on the results and therefore the AVCO equilibrium product distribution has been used as a basis for our calculations, adjusted to 0.5 wt % residual sulfur. Using the absorption reaction comprising 2 moles of NaAlO_2 yielding 1 mole of Na_2SO_4 plus 1 mole of Al_2O_3 , and the specified condition of 3 wt % S as regenerator feed, the moles of Na_2SO_4 and therefore the moles of Al_2O_3 formed in the absorber were calculated. This material balance calculation is illustrated in Appendix Table G-82.

AVCO's reformed gas composition has been adjusted somewhat to suit our conditions. The AVCO off-gas composition was then slightly adjusted in order to achieve the balanced

reaction. Table G-83 contains the balanced regeneration reaction along with the amount of regeneration gas needed corresponding to 80% utilization.

The regenerator was initially designed at 1200°F and 15 psig with 80% reducing gas utilization for a range of conditions, namely a superficial inlet gas velocity of 0.2-0.5 ft/sec, and a solids hold-up time of 1-4 hours. A maximum vessel diameter of about 40 ft was assumed and the bed density was taken to be 45 lbs/ft³ based on reported values.

Table 32 lists the specified regeneration conditions along with the various dimensions which have been calculated for these preliminary conditions. As can be seen from the table, the space velocity depends solely on the solids hold-up time, and the bed height is directly related to the hold-up time for each vessel diameter and superficial gas velocity. This it is apparent that several different combinations of gas velocity and vessel size can be used for the same space velocity. For our preliminary process design case, it was decided to choose a 2 hour hold-up time and a superficial inlet gas velocity of 0.3 ft/sec since this approximates an actual USBM 55,000 CFH pilot plant moving bed regeneration run*. To allow for process uncertainties, however, a 25% safety factor on height has been included. Additional allowances are needed for gas connections, disengaging height, etc., so 20 feet was added to the calculated bed height resulting in overall dimensions for each of the two regenerators, under the conditions of Table 32, of 33 feet diameter x 43 feet high.

* USBM Quarterly Report, Section I, March 31, 1968.

TABLE 32

MOVING BED REGENERATOR DESIGN--1000 MW PLANT

Temperature	1200°F	Reducing Gas	Reformed Natural Gas (76.9% H ₂ , 13.1% CO ₂ , 10% CO)
Pressure	15 psig	Reducing Gas Utilization	80%
Inlet Superficial Gas Velocity	0.2+0.5 ft/sec	Total Inlet ACFM	30,950
Solids Hold-up Time	1+4 hrs	Packed Solids Density	45 lbs/ft ³
		Total Solids Flow Rate	705,792 lbs/hr.

REGENERATOR DIAMETER AND BED HEIGHT AS A FUNCTION OF GAS VELOCITY AND HOLD-UP TIME

V_G (ft/sec)	Cross Sectional Area/ Vessel (ft ²)	No. of Vessels	Diameter	Hold-up Time (hrs)	Solids Volume/ Vessel (ft ³)	Space Velocity ft ³ gas/hr ft ³ solids	Bed Ht/ Vessel (ft)	Bed Ht @ 25% S.F. (ft)
0.2	1290	2	40'-6"	1	7,842	118.4	6.1	8
				2	15,684	59.2	12.2	15.5
				3	23,526	39.5	18.1	23
				4	31,368	29.6	24.4	31
0.3	860	2	33'	1	7,842	118.4	9.1	12
				2	15,684	59.2	18.2	23
				3	23,526	39.5	27.3	34.5
				4	31,368	29.6	36.4	46
0.4	1290	1	40'-6"	1	15,684	118.4	12.2	15.5
				2	31,368	59.2	24.4	31
				3	47,052	39.5	36.6	46
				4	62,736	29.6	48.8	61
0.5	1032	1	36'-3"	1	15,684	118.4	15.2	19
				2	31,368	59.2	30.4	38
				3	47,052	39.5	45.6	57
				4	62,736	29.6	60.8	76

Preliminary Case: 0.3 ft/sec superficial inlet gas velocity) 2 Regenerators each
2 hrs hold-up) 33'φ x 43' overall height

A heat balance around each of the regenerators showed the temperature of the outlet streams to be 1129°F, based on the following:

- All inlet streams at 1200°F.
- 80% utilization of regeneration gas.
- Heat of reaction is endothermic and equals about 509 cal/g mole Na_2SO_4 at 1200°F, based on the product distribution in Table G-83.
- 3 wt % S regenerator feed is regenerated to 0.5 wt % S
- All of the SO_2 removed from the flue gas is transferred to the regenerator off-gas.
- Heat loss based on a 25°F ambient temperature, a wind velocity of 20 miles/hr, and the regenerator size, preliminary case, specified in Table 32.

The calculated heat of reaction for the assumed regeneration reactions is endothermic, but because of the small number of moles reacting compared to the total flow rate, its effect on the overall heat balance is small. Therefore, the major factor contributing to the temperature decrease during regeneration for this particular design is the estimated heat loss.

In these preliminary process design calculations, regeneration has been assumed to occur at 1200°F, based on Bruceton pilot plant data. The heat of reaction calculated depends on both the reaction temperature and the regeneration reaction (i.e., product distribution). In our regeneration calculations the reaction used was that obtained from the 16th Monthly AVCO report, April 29, 1968, and adjusted for our conditions, it should be noted that adjusting the product distribution caused the heat of reaction to change from exothermic to endothermic. This calculated heat of reaction at

1200°F was used in the regenerator heat balance from which an outlet solids temperature of 1129°F was obtained. In order to maintain the regenerator at a minimum of 1200°F, the solids heater duty must have additional heat for a ΔT of 71°F, i.e., the solids enter the regenerator at 1271°F and cool to 1200°F by the time they are discharged. Therefore, the solids heater duty must be capable of heating the solids from 600-1271°F. Since there is some doubt as to which of several possible regeneration reactions is the correct one, it is desirable to know what effect each of the different reactions would have on the heater design. This has been done as described below.

Table 33 lists heats of reaction at 1200°F for various regeneration reactions. Each of these heats of reaction has been used in the regenerator heat balance, other conditions remaining the same, to calculate the outlet temperature in each case. Table 33 summarizes the results of the preceding calculations and shows that, based on a 1200°F regeneration temperature, the outlet solids temperature will vary from 946 to 1278°F, depending on which of the several regeneration reactions is used. Therefore, it can be seen that it is important to know which of the various regeneration reactions is applicable so that the solids heater is designed for the duty required to maintain the desired regeneration temperature.

(4) Solids Heater

Since sorption occurs at 600°F and regeneration at 1200°F, heating and cooling of the solid sorbent particles through a 600°F range is required for each sorption-regeneration cycle. Thus heat exchange between solids and gases comprises a major process step; however, no experimental data have been reported for this operation by the various alkalized alumina investigators, and it is necessary to design

TABLE 33

EFFECT OF THE HEAT OF REACTION ON THE REGENERATOR HEAT BALANCE

EQUATION*	MWK ΔH_R @ 1200°F (kcal/g mole)	Calculated Re- generator Outlet Temp** (°F)	Regenerator ΔT from base of 1200°F (°F)
1. $\text{Na}_2\text{SO}_4 + 4\text{H}_2 + \text{Na}_2\text{O} + \text{H}_2\text{S} + 3\text{H}_2\text{O}$	44.9	946	-254
2. $\text{Na}_2\text{SO}_3 + \text{Al}_2\text{O}_3 + 3\text{H}_2 + 2\text{NaAlO}_2 + \text{H}_2\text{S} + 2\text{H}_2\text{O}$	-11.7	1179	- 21
3. $\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 4\text{H}_2 + 2\text{NaAlO}_2 + \text{H}_2\text{S} + 3\text{H}_2\text{O}$	0.83	1127	- 73
4. $\text{Na}_2\text{SO}_4 + 4\text{CO} + \text{H}_2\text{O} + 4\text{CO}_2 + \text{H}_2\text{S} + \text{Na}_2\text{O}$	12.6	1079	-121
5. $\text{Na}_2\text{SO}_3 + \text{Al}_2\text{O}_3 + 3\text{CO} + \text{H}_2\text{O} + 3\text{CO}_2 + \text{H}_2\text{S} + 2\text{NaAlO}_2$	-35.8	1278	+ 78
6. $\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 4\text{CO} + \text{H}_2\text{O} + 4\text{CO}_2 + \text{H}_2\text{S} + 2\text{NaAlO}_2$	-31.3	1260	+ 60
7. AVCO† adjusted reaction used for preliminary process design calculations -- 1000 MW plant.	0.51	1129	- 71

1961

† 16th Monthly AVCO Report, 4/29/68, p. 50

* MWK Progress Report No. 4-5, Table 3, p. 29

** From preliminary process design regenerator heat balance calculations,
1000 MW plant, using the various equations ΔH_R .

the solids exchangers based on other information. To ascertain what information is available, a literature search was carried out for heat transfer correlations for gas-solid systems, particularly for the case of heat transfer to a moving bed of solids. The sources surveyed included the following:

- International Journal of Heat and Mass Transfer, Vols. 1-11
- ASME Index, 1940-1956
- Engineering Index, 1962, 1967
October 1968
- Theoretical Chemical Engineering Abstracts, 1964-1967
- Chemical Abstracts, 4th & 5th
Decennial 1937-1956, 6th Collective
1957-1961
- Assorted Review Articles

A review of the above sources showed that there is a paucity of design information in the published literature relating to equipment for transferring heat to or from granular (i.e., nonfluidized) materials. To further complicate matters, two of the correlations reported by different investigators give opposite results; i.e., one correlation shows bed height increasing as bed diameter increases whereas another correlation shows a decrease in bed height as bed diameter increases. However, all of the correlations used to calculate the effective exchanger length (defined as the axial length in which all of the heat is transferred) for moving bed exchangers give very short bed heights (i.e., 1-3 feet). The large volume of gases and solids being handled requires a very large cross-sectional area (6000 ft², equivalent to a vessel diameter of 88 feet) and the feed distribution systems will likely be very costly, particularly for the solids. Thus if the bed height calculated from the published heat transfer

correlations is increased by a 100% safety factor, the resulting increase in vessel cost will probably be small compared to the total cost. Therefore, the time and cost of an experimental program to obtain heat transfer data does not appear to be justified.

Process calculations for the regeneration solids heater are described on the following page.

The solids heater duty was calculated to be 75.6 MM Btu/hr/train based on the following conditions:

- Regenerator feed heated from 600→1271°F. The regenerator is to operate at a minimum temperature of 1200°F and the additional 71°F ΔT is necessary to maintain this temperature based on the regenerator heat balance.
- One exchanger train required for each regenerator, or a total of 2 trains.
- Heat loss based on an assumed ΔT of 100°F, wind velocity of 20 miles/hr, and an estimated solid heater size, was essentially negligible in comparison to the required duty. For calculation purposes, the heater vessels are assumed to be cylinders.
- The duty specified above, 75.6 MM Btu/hr for each of 2 trains, includes a 10% excess over theoretical for process uncertainties.

To avoid sintering of the sorbent particles, the maximum allowable inlet gas temperature to the solids heater was assumed to be 1500°F. With the inlet temperature fixed, the required amount of gas necessary to satisfy the duty will vary with the exit gas temperature. The vessel diameter in turn is dependent on the actual gas flow rate (hence pressure, since temperature is fixed) and the superficial gas velocity. For this particular case, a 10°F and

50°F approach (outlet gas-inlet solids) was chosen, along with a 0.5 ft/sec average superficial gas velocity. Therefore, assuming a 1 psig pressure drop through the exchanger, the variation of cross sectional area, and hence diameter, with pressure can be calculated. A sample calculation of the solids heater diameter for a 2 psig inlet pressure and a 10°F and 50°F approach is tabulated in Table G-84. Vessel diameters have also been calculated for various assumed pressures and the results are shown in Figure 48 along with the required bed height for each case. (The method of calculating bed height is discussed later on.) Calculations indicate that the smaller temperature approach, namely 10°F, will be more economical yielding a lower required gas flow rate and hence a smaller vessel diameter. The 50°F temperature approach case has been included in the event that a 10°F approach cannot be achieved in the actual exchanger.

With duty, gas flow rate, and vessel diameter specified, the remaining unknown is the required solids bed height necessary to accomplish the desired heat transfer. As previously mentioned, the published literature contains relatively little design information relating to the case of countercurrent heat transfer between a flowing gas and a moving bed of solids but some information is available. Using the information obtained from the literature, the required bed height for several different cases has been calculated. The pertinent references are discussed below.

- "Heat Transfer to Granular Materials-Settled Beds Moving Downward through Vertical Tubes," Brinn, M.S., Friedman, S. J., Gluckert, F. A., & Pigford, R. L., IEC, 40, 1050 (1948).
- The method for transferring heat to the granular solid consisted of passing the granular material, as a settled bed, downward through vertical jacketed tubes. Data

FIGURE 48
SOLIDS HEATER

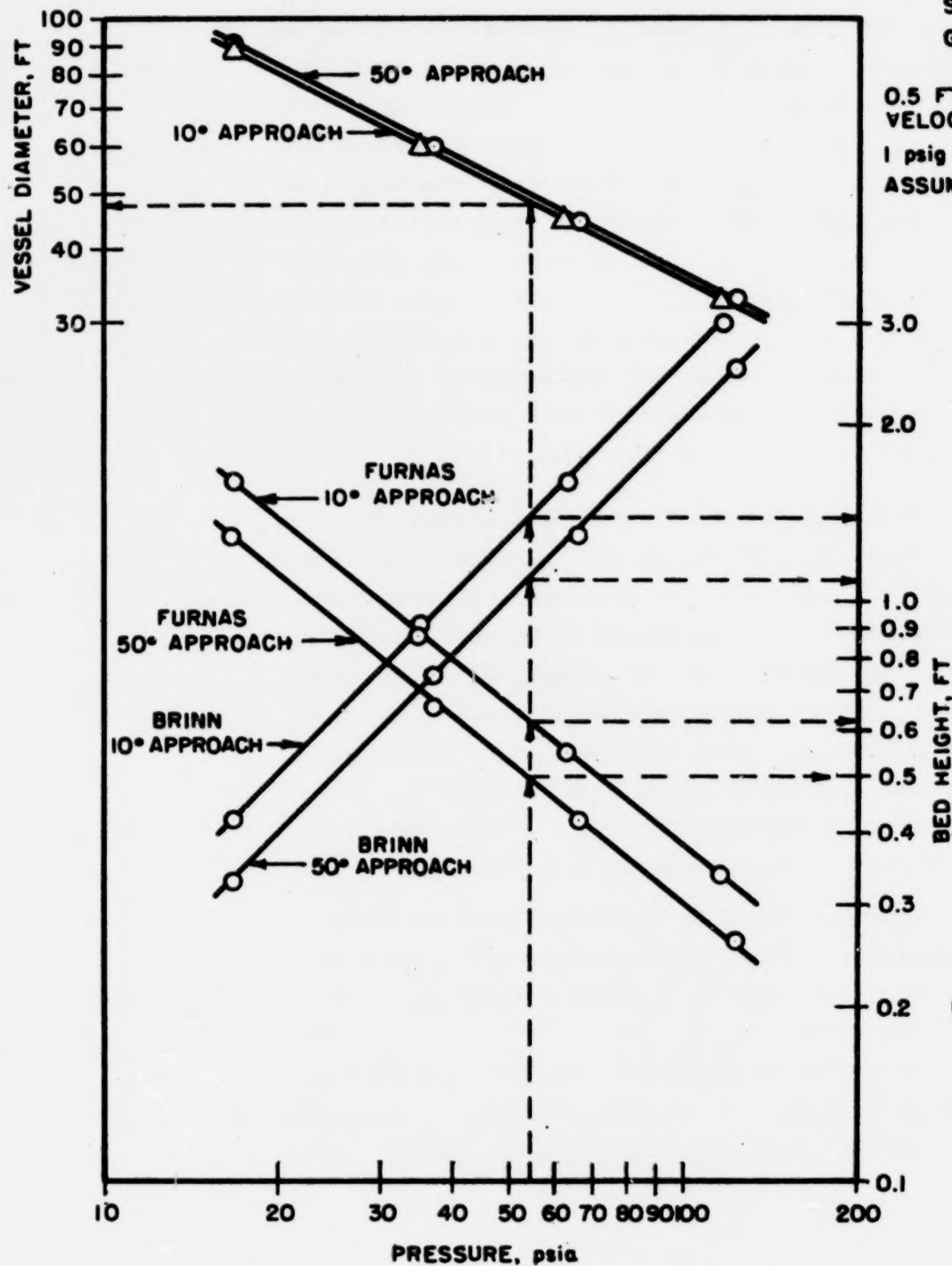
VESSEL DIAMETER AND BED HEIGHT
VS
PRESSURE

2 TRAINS REQUIRED
75.6 mm BTU/HR/TRAIN

10° APPROACH:
SOLIDS - 600 → 1271F
GAS - 610 ← 1500F

50° APPROACH:
SOLIDS - 600 → 1271F
GAS - 650 ← 1500F

0.5 FT/SEC AVERAGE GAS
VELOCITY
1 psig PRESSURE DROP
ASSUMED



REFERENCES:

1. Brinn, M.S., et al., *Ind. Eng. Chem.*, **40**, 1050 (1948).
2. Munro, W.D. and Amundson, N.R., *Ind. Eng. Chem.*, **42**, 1481 (1950).

collected indicated that the beds moved substantially as rods. It was shown that heat transfer to fluids in rodlike flow in a tube is mathematically identical to the unsteady state heating of a long cylinder with negligible surface resistance. Theoretical equations were developed and design charts prepared for the general case of countercurrent heat transfer to a material in rodlike flow in a tube. Equations were also developed for the case of parallel flow.

The design charts presented are plots of the Graetz Number ($w c_p / kL$) vs a temperature ratio, with a parameter B , defined as the ratio of the resistance to heat flow of the jacket fluid to the granular material. These charts are given for three values of z , defined as:

$$\frac{w c_p}{W C_p} \text{ where}$$

w = solids weights flow rate per tube
 W = jacket fluid weight flow rate per tube
 c_p = solids specific heat
 C_p = jacket fluid specific heat

Examples are shown for a particular set of heat transfer conditions, illustrating the use of the design charts in calculating the required flow rate per tube and, from this and the total solids flow rate, the total number of tubes required.

Although heat is transferred in the present tentative design of the solids heater by direct countercurrent contact of gas and solids, rather than indirectly through jacketed tubes, a modified calculation procedure can be developed for our

particular case. That is, the correlation can be used to calculate the total tube length required for our set of conditions and depending on the number of tubes required, which is obtained directly as a function of vessel diameter, tube spacing, and pitch, the required bed height can then be calculated. This procedure is tabulated in Table G-85 for the low pressure, 90.5 ft diameter, 50°F approach case. Other calculations were done for lower diameter and higher pressures for both a 50°F and 10°F approach and these results are plotted on Figure 48. For a given pressure, the bed height and vessel diameter can be determined for the two temperature approaches. The Brinn correlation predicts an increase in bed height with a decrease in vessel diameter and the 10°F approach predicts a slightly higher bed height than the 50°F approach for a comparable pressure. The actual calculated bed heights range from 0.33 feet to 3 feet for the pressure-diameter-temperature approach spread studied as indicated on Figure 48.

"Solid-Fluid Heat Exchange in Moving Beds", Munro, W. D. and Amundson, N. R., IEC, 42, 1481 (1950).

The problem of heat exchanger was considered for the case in which the solid is in the form of uniform spheres. The resistance to heat transfer by conduction in the solid was taken into consideration. It was assumed that conduction in the fluid in the direction of flow is negligible and that the exchanger itself is adiabatic, so that no temperature gradient

in a radial direction in the fluid exists. An exact solution of the theoretical equations involved in the problem of heat exchange between solid and fluid was developed for both parallel and counterflow exchangers. The authors felt that in some cases the assumption by other investigators of negligible resistance to heat transfer by conduction in the solid could lead to an undersizing of exchanger length. However, the equations presented require a computer program for use, and it appears that the assumption of negligible resistance to heat transfer within the particles is valid provided the particles which make up the bed are small enough and have a sufficiently high thermal conductivity. Therefore, it was decided to use an approximate method, referred to in the article, for the calculation of bed height.

The Furnas* approximate solution considered the case in which conduction in the solid is neglected and the problem is considered as an ordinary countercurrent heat exchanger in which the area for heat exchange is the total external area of the particles in the bed at one time. This method is outlined, along with a sample calculation, in Table G-86 for the low pressure, 90.55 ft diameter, 50°F approach case. Included in Figure 48 is the variation in bed height, determined by the Furnas approximate equation, as a function of pressure and vessel diameter for both a 50°F approach and 10°F approach. For a comparable pressure, the 10°F approach predicts a slightly higher bed height than

* Furnas, C. C., IEC, 22, 26 (1930)
Furnas, C. C., TRANS AICHE, 24, 1942 (1930)
Furnas, C. C., US. BUR. MINES, BULL. 361 (1932)

the 50°F approach, as does the Brinn correlation. However, the Furnas equation predicts an increase in bed height with an increase in diameter, which is the reverse of the height-diameter relationship obtained from the Brinn correlation. The Furnas equation (Table G-86) indicates that the temperature ratio

$$\left(\frac{T-t_o}{T_o-t_o} \right)$$

is a function of the exponential ratio of the product of the heat transfer coefficient at the solid-fluid interface (h_f) and the bed height (x) to the solids mass velocity (G_s):

$$(T-t_o)/(T_o-t_o) = f(\exp [(h_f/G_s) x])$$

The correlation used to calculate heat transfer coefficients used in the Furnas equation is the one developed by Leva and is shown in Table G-86. It is possible that other correlations for calculating heat transfer coefficients might produce a different relationship between bed height and diameter as predicted by the Furnas equation, but the Leva correlation has been used here since it is generally accepted as a valid correlation. As can be seen from Figure 48, the bed heights calculated using the Furnas method range from 0.26 feet to 1.6 feet for the pressure-diameter-temperature approach spread studied, vs a 0.33 feet to 3 feet range predicted by the Brinn correlation for the same process conditions.

M. W. Kellogg Correlation

This correlation is used for calculating the temperature history curves during heating of a

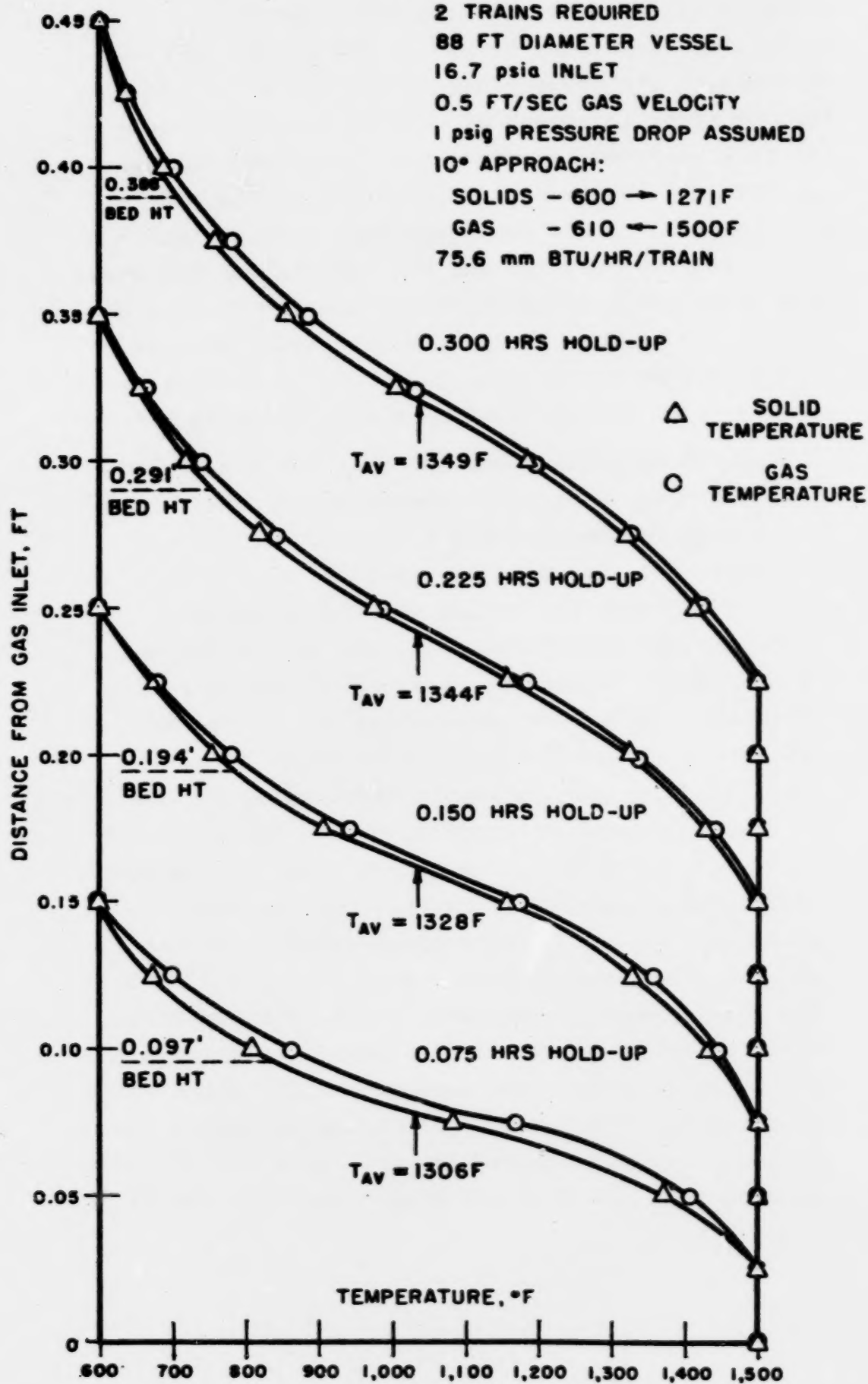
fixed bed of solid particles. The calculation consists of first determining the convection coefficient and then, by use of the design charts, determining the temperature at several points in the bed after an amount of heating gas corresponding to a selected time interval has passed through the bed. If the average temperature of the bed so calculated is not that required, another interval of time is selected and the calculation repeated. This calculation is intended for use in the case of a fixed bed and not a slowly moving bed. However, it was decided to use this procedure in the following variation for the case of a slowly moving bed:

Assume it is a fixed bed and that for a specific hold-up time, a definite amount of material would be placed in the vessel and allowed to come to equilibrium. Various hold-up times were then chosen and from the solids flow rate, packed density, and vessel diameter, the bed height was calculated. Temperature history curves were then plotted to determine at what bed height the desired average solids temperature would be 1271°F. Table G-87 contains a sample calculation for the 88 feet diameter, 10°F approach case for a hold-up time of 0.075 hours. The complete set of temperature history curves for various hold-up times and corresponding bed heights are plotted on Figure 49 for the low pressure case and in Figure G-92 for the high pressure case, both for a 10°F approach. (See Figure 48 for pressure-diameter relationship.) As can be seen from the average solids temperatures obtained for the corresponding hold-up times, the average required temperature of 1271°F was exceeded in less than a 1 foot bed height for both the 88

FIGURE 49
TEMPERATURE-HISTORY CURVES FOR SOLIDS HEATER

MWK METHOD

2 TRAINS REQUIRED
88 FT DIAMETER VESSEL
16.7 psia INLET
0.5 FT/SEC GAS VELOCITY
1 psig PRESSURE DROP ASSUMED
10° APPROACH:
SOLIDS - 600 → 1271F
GAS - 610 ← 1500F
75.6 mm BTU/HR/TRAIN

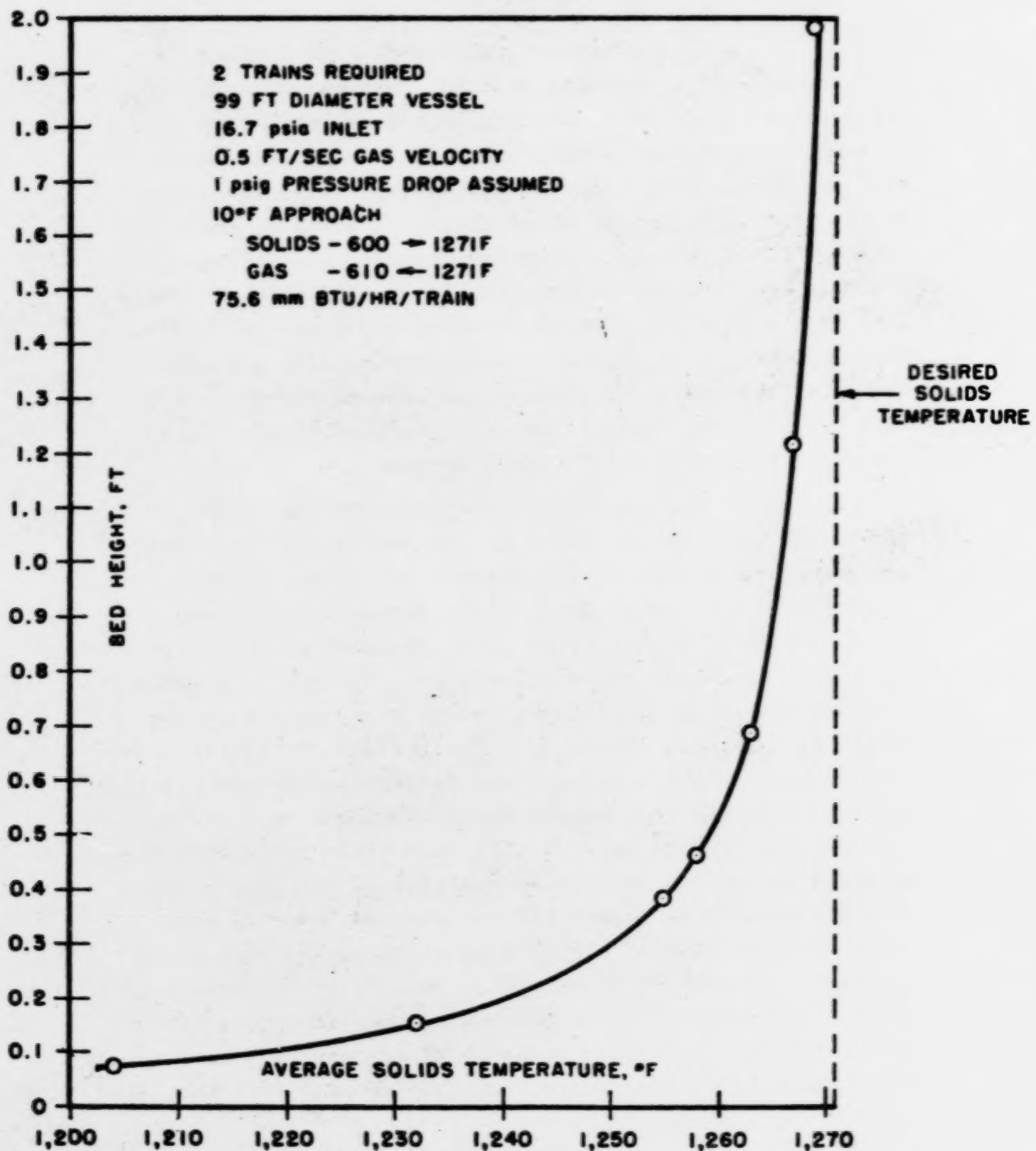


feet (low pressure) and 33 feet (high pressure) diameter case.

In all previous discussed calculations, a pressure drop of 1 psig was assumed. Happel, J., IEC, 41, 1161 (1949) developed a correlation for pressure drop due to vapor flow through moving beds. The correlating equation was obtained by applying the Navier-Stokes equations to the viscous motion of fluid through a group of uniform spheres. Flow through a granular material was accounted for by a new function of the fractional void volume. Table G-88 is a sample calculation for pressure drop for the 90.5 feet diameter, 50°F approach case. The results indicate that for the conditions studied, an assumed pressure drop of 1 psi is sufficient, since this provides an additional 0.5 psi for the gas distribution system.

The inlet gas temperature to the solids heater was taken to be 1500°F in the previous calculation and consequently part of the sorbent was heated to this temperature. In the event that the sorbent temperature might have an allowable upper limit of about 1300°F (e.g., to avoid sintering), an additional case has been evaluated in which the inlet gas temperature is fixed at the outlet solids temperature, namely 1271°F. The MWK correlation was used to calculate the average solids temperature for specific hold-up times and bed heights for a low pressure, 10°F approach case. Figure 50 is a plot of the average solids temperature vs bed height, and indicates that the required bed height necessary to accomplish the desired heat transfer (solids heated from 600→1271°F) is small, being only about two feet. As the bed height is increased, the average solids temperature rapidly approaches and becomes asymptotic to 1271°F for the conditions chosen. After only two feet, however, the solids temperature is within about 2°F of the inlet

FIGURE 50
AVERAGE SOLIDS TEMPERATURE VS BED HEIGHT



gas temperature so by increasing the inlet gas temperature by two degrees, the desired solids temperature could be obtained.

b. Vessel Design

(1) Absorber

A material balance, Table G-89, around the 600°F dispersed phase absorber establishes the inlet and outlet flow rates. A heat balance around the absorber showed the temperature of the outlet stream to be 603°F, based on the following:

- All inlet streams at 600°F
- Heat of reaction is -115.7 kcal/g mole SO_2 at 600°F, assuming sorbent is NaAlO_2
- 90% removal of sulfur oxide in entering gas.
- Heat loss based on an assumed ΔT of 300°F (i.e., vessel wall temperature of -325°F), wind velocity of 20 miles per hour, and an estimated absorber size.

Thus the temperature rise in the absorber is negligible due to combination of large flow rates and low concentration of SO_2 in the feed gas, hence relative small total heat release.

For the calculation of the absorber dimensions, 25 ft/sec was chosen as the inlet gas velocity and it was decided that initially the maximum specified diameter per vessel would be 40 feet. USBM Quarterly Report, Section I, March 31, 1968, included a series of equations relating the sorption rate constant with absorber height and other known quantities. Table G-90 is a consolidation of these equations into one equation explicit in column height, for the case of 90% SO_2 removal. A sample calculation for obtaining the absorber dimensions is included as Table G-91.

(2) Solids Heater

A major process step in the alkalized alumina process is heat exchange between solids and gases in each sorption-regeneration cycle since sorption occurs at 600°F and regeneration at 1200°F or higher. Previous calculations have indicated that a moving bed heater requires a very large cross sectional area, approximately 6000 square feet (~90 feet diameter), due to the low gas velocity of 0.5 ft/sec necessary to avoid fluidization. On the other hand, various correlations used to estimate the required bed height have indicated that this is very small, in the range of 3 feet or less. This combination of large diameter and extremely small bed height results in an impractical vessel design with very complicated and expensive gas and solid distribution systems. As a result of the above factors it was decided to evaluate other heat exchange systems.

A fluidized bed concept would permit the use of higher gas velocities, thereby decreasing the vessel diameter, and a direct combustion fluidized solids heater would minimize volumetric gas flow rate, thus further lowering the vessel diameter.

Therefore, it was decided to evaluate the use of a direct combustion fluidized bed design as the solids heater. Since at the time these calculations were made the process design included a solids cooler downstream of the regenerator, the optimization described below was for both the heating and cooling operation rather than only heating. Elimination of the solids cooler does not change the relative comparisons of the different cases, however, and the design selected for the heater also would be picked without the cooler. As a result of the fluidized bed study, a direct combustion fluidized bed heater was selected for the final design.

The regeneration temperature was originally set at 1200°F based on pilot plant data available at the time but later data indicated that it would be desirable to regenerate at a higher temperature, viz, in the range of 1300°F. Since it was shown that a direct combustion fluidized heater gave the lowest costs, and since the minimum temperature at which a direct combustion will occur without excessive carbon deposition is about 1400°F, it was decided to increase the regeneration temperature to this level. As indicated above, a regeneration temperature of about 1300°F would be satisfactory so it was not necessary to heat above 1400°F to allow for heat losses as was done with the 1200°F design. That is, if heat losses and/or endothermic heat of reaction caused the temperature to fall below 1400°F, reaction kinetics would not suffer as long as the regenerator did not drop below about 1300°F.

To determine the optimum (or nearly optimum) design for these heat exchange vessels, several schemes were evaluated, namely, various combinations of 1, 2, and 3-stage fluid bed heaters and coolers, and a direct combustion fluidized solids heater combined with either a 1, 2, or 3-stage solids cooler. Further, each combination was evaluated at pressure levels of 20, 30 and 50 psia. Final selection was based primarily on economics, calculated as follows.

For each scheme an energy balance and fuel requirement were calculated (based on a regeneration temperature of 1400°F in all cases) and preliminary vessel designs prepared from which the approximate capital investment was estimated. The annual cost of fixed charges was taken to be 15% of the erected plant cost. For utilities, natural gas was charged at 27¢/MM Btu* and electric power was assumed to be 5 mills/kwh.

* Average fuel cost for the U. S. as reported in "Steam-Electric Plant Factors -- 1968 Edition," published by the National Coal Association.

A stream efficiency of 60% or 5250 hours/yr was chosen as being a reasonable basis for a 1000 MW power plant upon which our evaluations are based. Total annual costs of each scheme were then calculated and, along with process operability considerations, used to select the optimum heating and cooling arrangement for the sorbent solids. Approximate capital investment and total annual cost for each scheme studies are tabulated in Table 34. Annual cost of fixed charges and total annual cost for the moving bed schemes were not included in Table 34 because of the impractical vessel requirements, as previously discussed. Of the remaining fluid bed cases studied, Table 34 indicates that the use of a 2-stage direct combustion fluid bed solids heater has a distinct economic advantage over the fluid bed heaters using externally heated gases as the source of heat. For the solids coolers, the total annual costs shown in Table 34 indicate that economics favor increasing the number of stages in the fluid bed solids cooler. The largest decrease in total annual cost occurs in going from 1-stage to 2-stage while a smaller decrease is evident in going from 2-stages to 3-stages. It can also be seen from Table 34 that an increase in pressure tends to increase the annual cost due to the larger compressor requirements.

It should be noted that both the investment and total annual costs shown in Table 34 are approximate in nature since detailed vessel designs were not made. For example, vessel costs were estimated directly from the approximate vessel weight with no allowance for additional incremental costs due to multiple beds. Likewise, secondary effects were neglected (e.g., running the regenerator system at about 30 psia eliminates the need to compress the gas stream feed to the Claus plant) since their influence on the total annual costs is probably not significant. Therefore, because of the approximate method of determining costs, small differences in the values shown in Table 34 should be neglected. Thus, a combination

COMPARISON OF VARI

Conditions:

- 1) Vessels - carbon steel with 1/2" thick wall.
- 2) 5 ft/sec average superficial gas velocity.
- 3) 1 psig pressure drop for fluid bed (FB) cases and 4 psig pressure drop for 2-stage direct combustion fluid bed (DCFB) cases.
- 4) Vessel heights calculated as follows:
 - 5 ft plenum chamber
 - 5 ft between beds
 - Bed height - For FB cases, 1 ft/stage, for 2-stage DCFB 10 ft for first stage and 1 ft for second stage.
 - Total Disengaging Height (TDH) taken as function of vessel diameter -

Ref: Frantz, J. F., CHEM. ENG., 69, 161 (1962)

ϕ , Vessel Diameter, (ft)	TDH (ft)
10	3.5 x ϕ
20	2 x ϕ
35	1 x ϕ

- 5) Cost figures chosen:
 - Carbon Steel - 50¢/lb
 - Natural Gas - 27¢/MM Btu;
 - Heating Value of 943.7 Btu/SCF
 - Electricity - 5 mills/KW-hr
- 6) 60% steam efficiency or 5250 hrs/yr

METHOD*	PRESSURE (PSIA)	SIZE	
		SOL. HTR.	ϕ x H (FT)
SH - 1 Stage FB ⁺⁺	20	55 x 61	
SC - 1 Stage FB ⁺⁺	30	44 x 50	
	50	34 x 40	
SH - 2 Stage FB	20	-	
SC - 2 Stage FB	30	-	
	50	-	
SH - 3 Stage FB	20	38 x 56	
SC - 3 Stage FB	30	31 x 58	
	50	24 x 59	
SH - 2 Stage DCFB	20	12 x 60	
SC - 1 Stage FB	30	10 x 54	
	50	7 x 46	
SH - 2 Stage DCFB	20	12 x 60	
SC - 2 Stage FB	30	10 x 56	
	50	7 x 56	
SH - 2 Stage DCFB	20	12 x 60	
SC - 3 Stage FB	30	10 x 56	
	50	8 x 47	

LEGEND

SH - Solids Heater
 SC - Solids Cooler
 FB - Fluid Bed
 MB - Moving Bed
 DCFB - Direct Combustion Fluid Bed

TABLE 34

COMPARISON OF VARIOUS DESIGNS FOR HEATING AND COOLING SOLIDS IN REGENERATION SECTION

		(1)		(2)		(3)				
PRESSURE (PSIA)	SIZE SOL. HTR. SOL. COOL. φ x HT. (FT)	TOTAL WT. (M LBS.)	ERECTED [†] PLANT COST (M \$)	FIXED CHARGES ANNUAL COST** (M \$/YR)	FUEL (MPH N.G.)	ANNUAL FUEL COST (M \$/YR)	COMP. BHP	ANNUAL ELEC. POWER COST (M \$/YR)		
FB ^{††}	20	55 x 61	24 x 47	552	820	124	1080	519	13,300	260
FB ^{††}	30	44 x 50	19 x 45	378	567	85.1	"	"	23,230	455
	50	34 x 40	15 x 47	244	366	54.9	"	"	38,700	758
FB	20	-	-	--	-	-	840	403	-	-
FB	30	-	-	-	-	-	"	"	-	-
	50	-	-	-	-	-	"	"	-	-
FB	20	38 x 56	20 x 58	366	549	82.4	520	250	5,100	100
FB	30	31 x 58	16 x 60	289	434	65.1	"	"	10,100	198
	50	24 x 59	12 x 56	208	312	46.8	"	"	17,000	333
DCFB	20	12 x 60	25 x 48	197	296	44.4	263	126	6,500	127
FB	30	10 x 54	20 x 46	144	216	32.4	"	"	11,300	221
	50	7 x 46	16 x 48	105	158	23.7	"	"	18,800	368
DCFB	20	12 x 60	21 x 52	178	267	40.1	240	115	3,600	70.
FB	30	10 x 56	17 x 53	139	209	31.4	"	"	6,200	121
	50	7 x 56	13 x 52	98	147	22.1	"	"	10,300	202
DCFB	20	12 x 60	20 x 58	181	272	40.8	232	111	3,000	58.
FB	30	10 x 56	16 x 60	142	213	32.0	"	"	5,200	102
	50	8 x 47	12 x 56	96	144	21.6	"	"	8,700	170

Solids Heater

Solids Cooler

Fluid Bed

Moving Bed

Direct Combustion Fluid Bed

* Regeneration temperature is 1400°F unless noted otherwise.

** 15% of erected plant cost/year.

† 3 x basic equipment cost

†† For regeneration temperature of 1200°F; 1400°F case would be hi

TABLE 34

DESIGNS FOR HEATING AND COOLING SOLIDS IN REGENERATION SECTION

	(1)			(2)		(3)		
COOL.	TOTAL WT. (M LBS.)	ERECTED [†] PLANT COST (M \$)	FIXED CHARGES ANNUAL COST** (M \$/YR)	FUEL (MPH N.G.)	ANNUAL FUEL COST (M \$/YR)	COMP. BHP	ANNUAL ELEC. POWER COST (M \$/YR)	TOTAL ANNUAL COST = (1 + 2 + 3) (M \$/YR)
47	552	828	124	1080	519	13,300	260	1464
45	378	567	85.1	"	"	23,230	455	1165
47	244	366	54.9	"	"	38,700	758	1893
	--	-	-	840	403	-	-	> 403
	-	-	-	"	"	-	-	"
	-	-	-	"	"	-	-	"
68	366	549	82.4	520	250	5,100	100	432
60	289	434	65.1	"	"	10,100	198	513
66	208	312	46.8	"	"	17,000	333	630
8	197	296	44.4	263	126	6,500	127	297
6	144	216	32.4	"	"	11,300	221	379
8	105	158	23.7	"	"	18,800	368	518
2	178	267	40.1	240	115	3,600	70.5	226
3	139	209	31.4	"	"	6,200	121	267
2	98	147	22.1	"	"	10,300	202	339
8	181	272	40.8	232	111	3,000	58.7	211
0	142	213	32.0	"	"	5,200	102	245
6	96	144	21.6	"	"	8,700	170	303

Regeneration temperature is 1400°F unless noted otherwise.

15% of erected plant cost/year.

3 x basic equipment cost

For regeneration temperature of 1200°F; 1400°F case would be higher

was selected for the present dispersed phase design (viz., a 2-stage direct combustion heater and a 2-stage solids cooler, both operating at 30 psia), that does not have the lowest annual costs, but the difference between it and the combination with the lowest total annual cost is relatively small. Further, the combination selected does exhibit the lowest investment compared to the other combinations that have lower annual costs, and it also has the advantage of easier operation: two beds instead of three in some cases, or no need for a compressor on the regenerator off-gases in other cases. Therefore, in terms of both economic and practical considerations, the best regenerator heat exchange arrangement for the present design was the one mentioned above, i.e., a 2-stage direct combustion fluid bed solids heater is combination with a 2-stage fluid bed solids cooler, both operating at 30 psia. A preliminary vessel design calculation for this combination is illustrated in Table G-92.

As previously noted, the above discussion and the sample calculation shown in Table G-92 are for the process design which included a solids cooler. In the final base case design the cooler was deleted which caused the heater duty to increase (preheated air was no longer available) and resulted in increased gas flow rates and slightly different vessel dimensions. The preliminary design discussed above produced a heater which was 10 feet in diameter by 56 feet high whereas the final design required 11 feet by 45 feet vessel. A sketch of the final design of the heater is shown in Appendix G, Figure G-94.

In the previous discussed heat transfer calculations involving a fluid bed concept, the bed height was assumed to be one foot per stage. Literature articles, in general, have indicated that heat transfer in a gas fluidized bed occurs over a very shallow portion of the bed and that the axial length in which all of the heat is transferred is very short. Temperature homogeneity is one of the characteristics of a fluidized bed and it is believed that heat transfer takes place almost instantaneously.

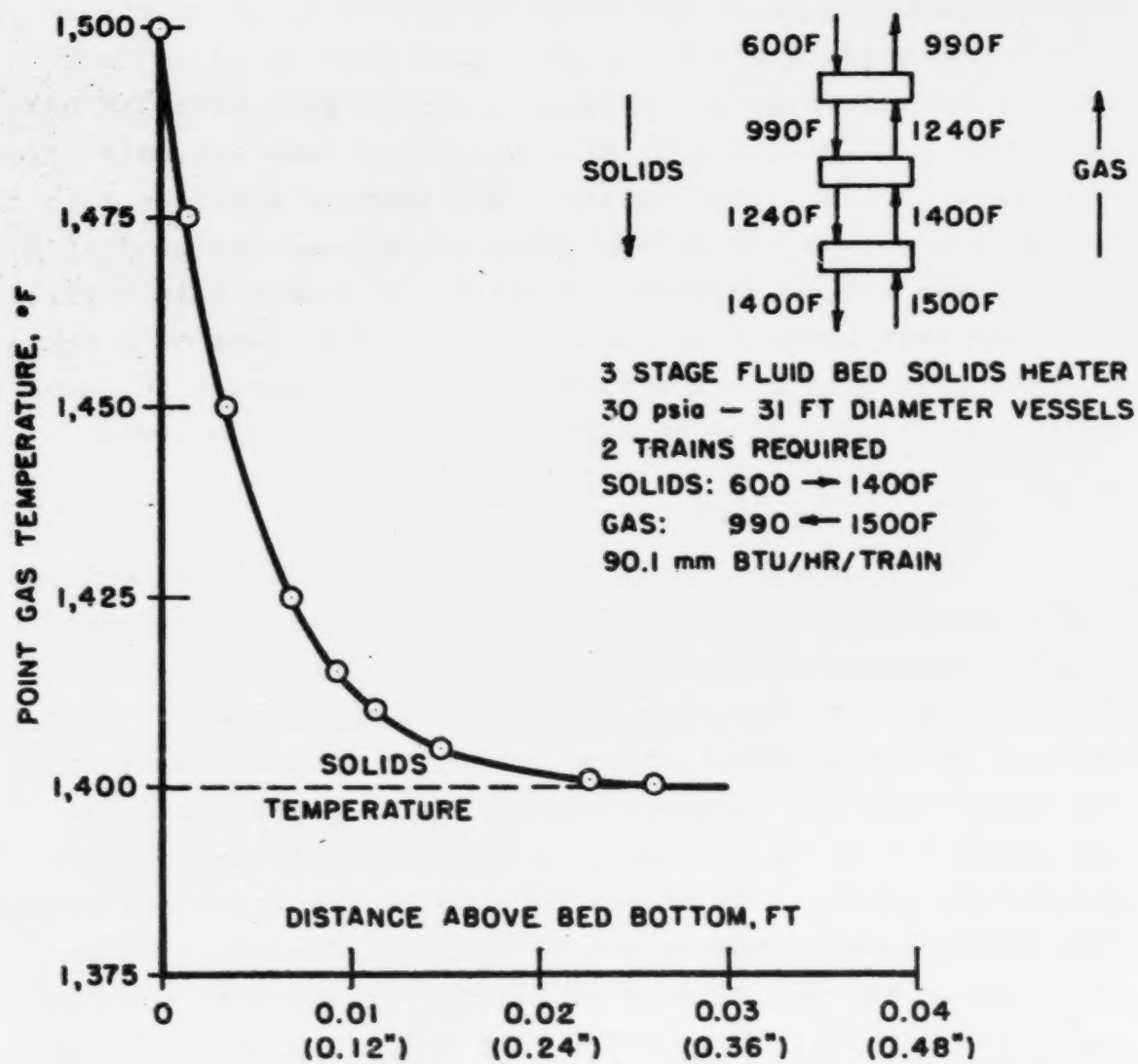
As a numerical check to see if the allowed one foot per stage bed height was sufficient, a calculation was made to estimate the bed height required for a specified heat transfer rate. Table G-93 shows a sample calculation for a 3-stage fluid bed solids heater with the temperature profile for the first stage plotted in Figure 51. It is evident from Figure 51 that the desired heating of the solids to 1400°F by 1500°F inlet gas can be accomplished in a bed height of less than 0.3 inch per stage, well under the assumed height of one foot per stage.

(3) Regenerator

Regeneration of the loaded sorbent is assumed to take place in a moving bed regenerator, similar to the one presently used in the USBM pilot plant at Bruceton. Process calculations and several different vessel configurations for the regenerator were discussed previously (Table 32). The preliminary calculations were made for a regeneration temperature of 1200°F whereas the final vessel design is based on 1400°F and consequently has slightly different dimensions than those shown in Table 32, viz, final dimensions are 35 feet diameter by 36 feet straight section (59 feet overall) vs. 33 feet x 43 feet preliminary size.

Since relatively little regeneration data are presently available, only tentative designs can be made at this time and assumptions are required for space velocity, reaction temperature, hold-up time, and superficial gas velocity. For the present design it has been assumed that for a nominal 1400°F regeneration temperature and 0.3 foot per second gas velocity, a two hour hold-up time is required. However, the regenerator has been designed so that solids hold-up time can be increased to three hours if necessary to obtain the specified level of regeneration: i.e., 0.5%

FIGURE 51
FLUIDIZED BED TEMPERATURE PROFILE
(FIRST STAGE)



REFERENCE:
 Frantz, J.F., *Chem. Eng. Prog.*,
 57, No. 7, 35 (1961).

sulfur at exit. The cost of the extra vessel height to obtain the additional one hour hold-up is small and therefore the overall regenerator cost is increased only slightly. The flexibility provided by the additional hold-up time is felt to justify the extra cost.

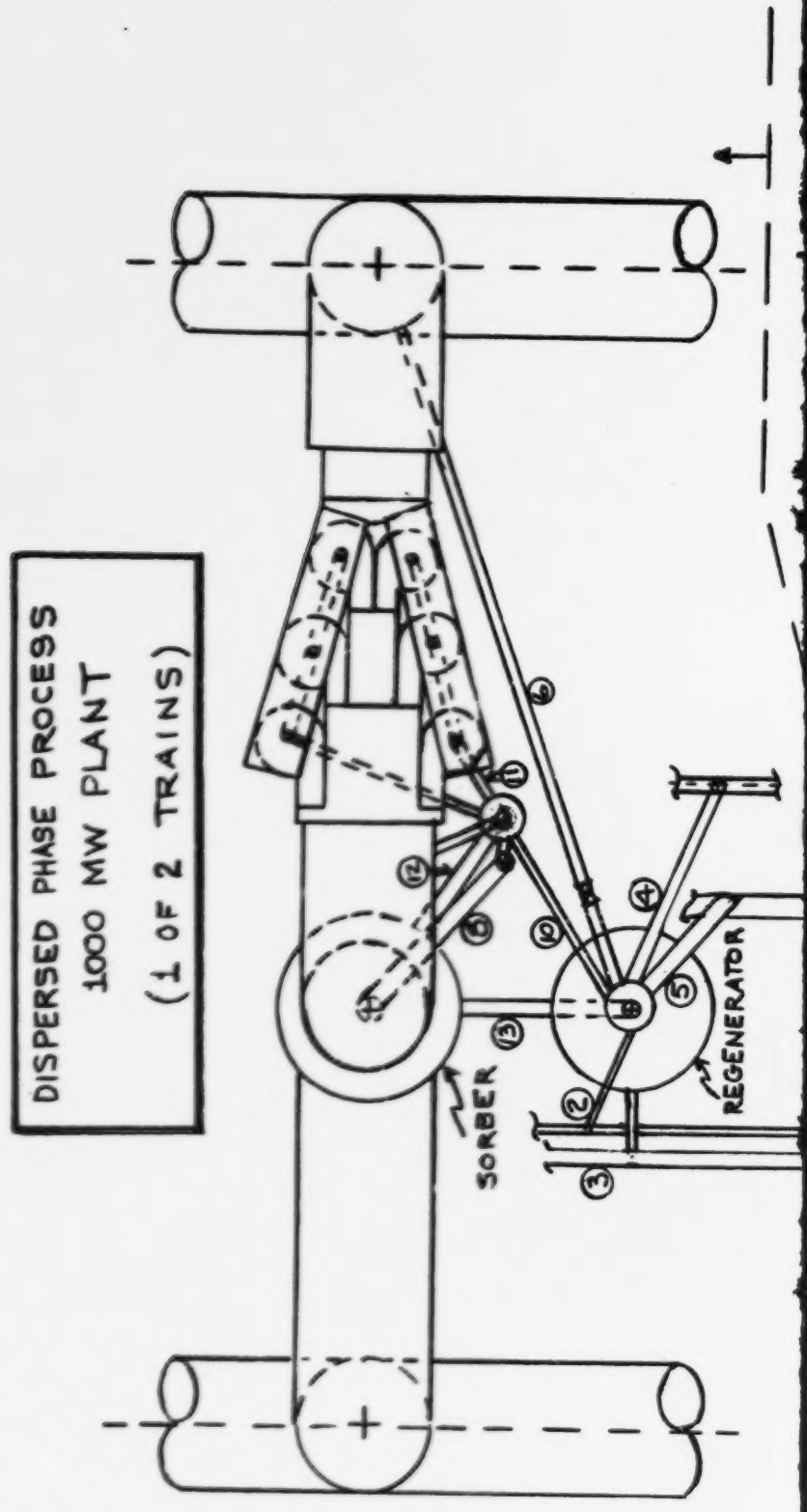
(4) Solids Transfer Lines

The transfer of sorbent particles between the reactor and regenerator (and vice versa) is done pneumatically, using dilute phase gas-solid mixtures. Line sizes and transport gas requirements have been calculated based on throughput solids loadings of one pound per cubic foot (derived from erosion considerations), whereas pressure drop calculations have used a slip factor of two, which has been estimated from the particle size distribution. The recycle transfer line from the bottom of the top of the reactor has been designed as a dense phase system, however, since it is essentially a vertical line and very large flow rates are involved. Use of a dense phase system with its lower velocity should result in lower sorbent attrition rates than a high velocity dilute phase system.

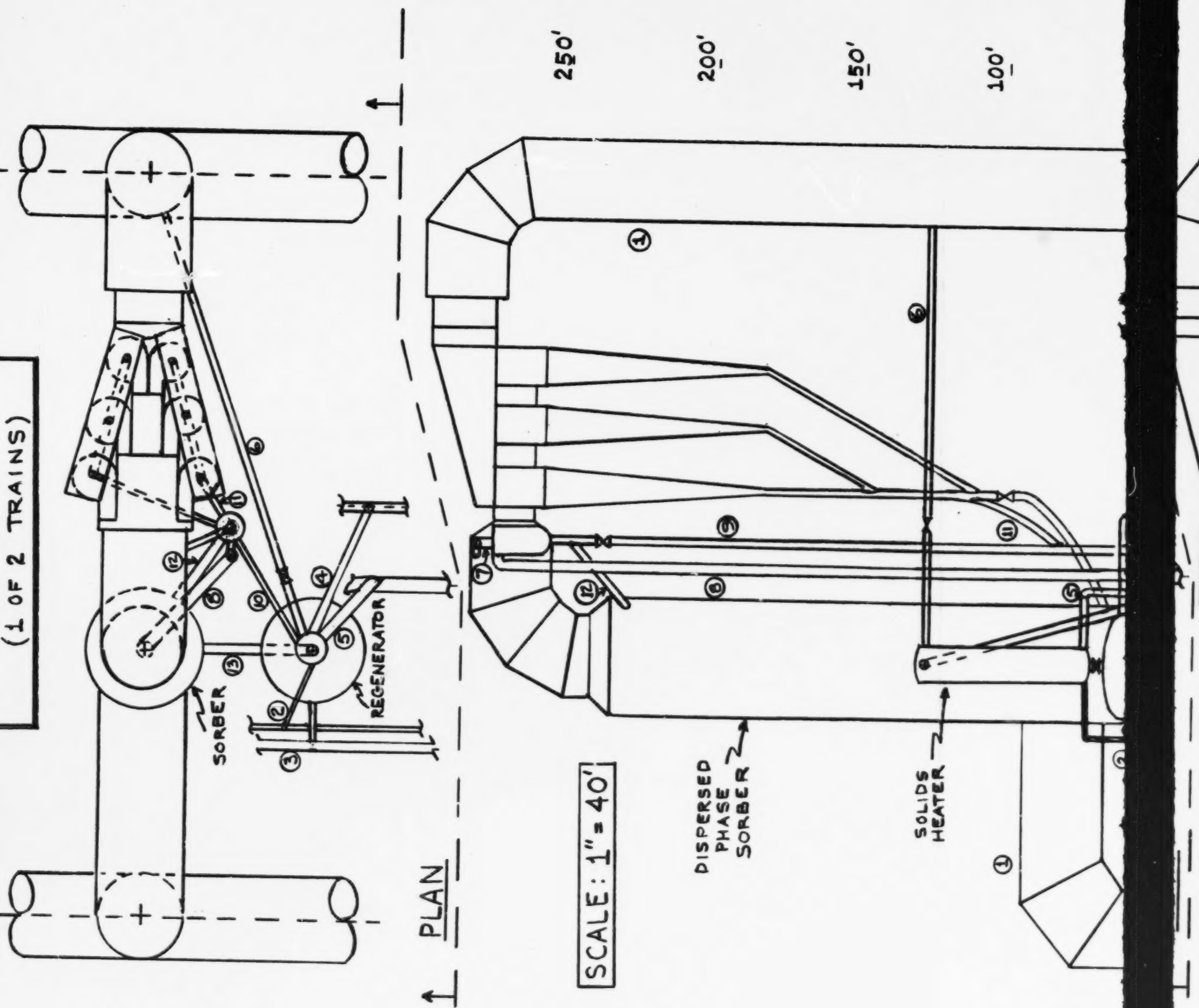
(5) Plant Layout

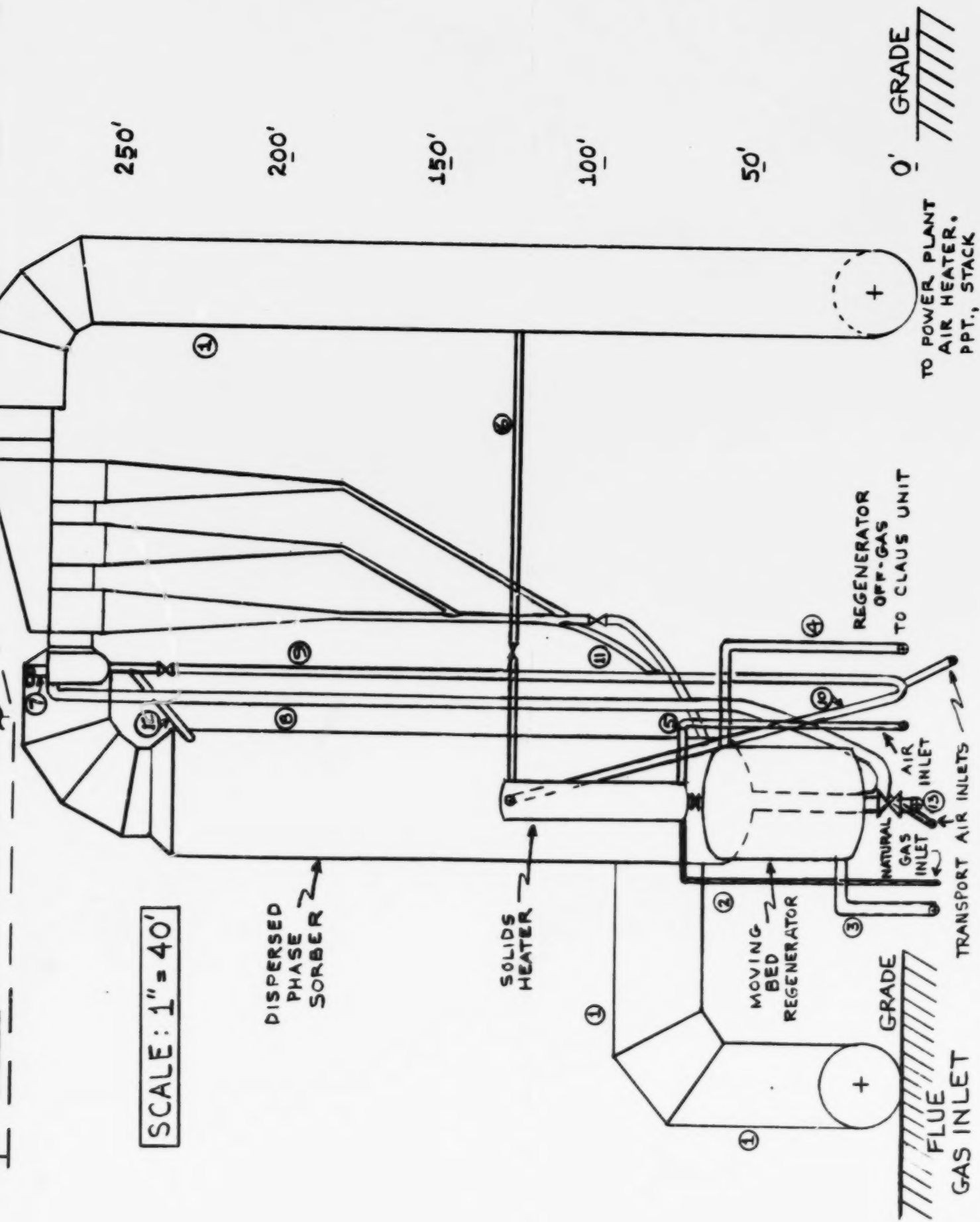
A rough layout of the process equipment was prepared in order to ensure a feasible basis for the estimate of plant investment and process economics. The layout is required because of the unusual nature of the process. That is, because of the extremely large volume of gases being handled, the very large gas ductwork required is a major cost item and therefore it is necessary to determine the approximate quantities needed. By preparing a rough layout of the process, the ductwork requirements can be readily obtained, and in addition, a better estimate of piping, structures, foundations, etc., can be made. Figure 52 shows the plan and elevation for one train of equipment and Figure 53 is a plant layout for

FIGURE 52
EQUIPMENT LAYOUT



(1 OF 2 TRAINS)





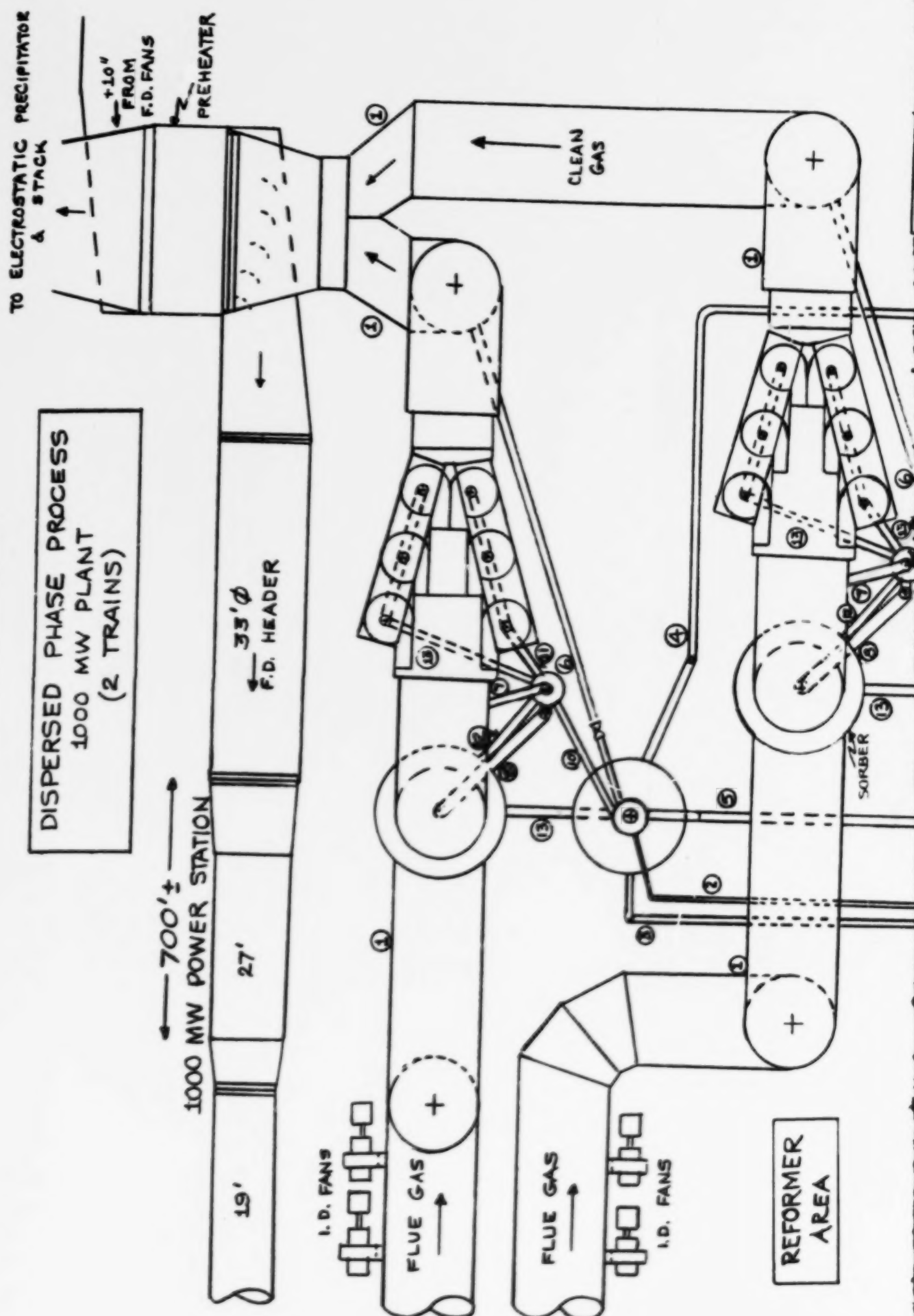
ELEVATION

SCALE: 1" = 40'

2

FIGURE 53

PLOT PLAN



PREHEATER

1000 MW POWER STATION

19'

27'

33' Ø
F.D. HEADER

I.D. FANS

FLUE GAS

FLUE GAS

I.D. FANS

CLEAN
GAS

REFORMER
AREA

CLAUS PLANT
AREA

2 NATURAL
GAS INLETS

3 REGENERATION
GAS INLETS

5 AIR
INLETS

REGENERATOR
OFF-GAS ⑤

REGENERATOR
SOLIDS HEATER

SCALE: 1" = 40'

TABLE 35

IDENTIFICATION OF LINES ON LAYOUT SKETCHES - FIGURES 52 AND 53
DISPERSED PHASE SORPTION - MOVING BED REGENERATION PROCESS SCHEME

<u>LINE NO.</u> <u>(FIGURES 52 & 53)</u>	<u>DESCRIPTION</u>
1	Ductwork - Flue Gas Inlet & Clean Gas Outlet
2	Natural Gas Inlet to D-2 Solids Heater
3	Regeneration Gas Inlet
4	Regeneration Off-Gas TL.
5	Air Line from Compressor J-1 to Solids Heater D-2
6	Flue Gas from D-2 Solids Heater to Clean Flue Gas Duct
7	Gas TL Gas-Solids Separator (L-2) to Clean Flue Gas Duct
8	Sorber Solids (Dense Phase) TL to L-2
9	L-2 Solids Outlet Standpipe
10	Solids Transfer Line from Grade to D-2 Solids Heater
11	L-1A-L-1F Cyclone Cluster Solids Outlet to Standpipe
12	Sorber Solids Recycle Line from L-2
13	D-3 Regenerator Solids TL to sorber

Note: TL = transfer line

2 trains. The pipe and ductwork numbered on Figures 52 and 53 are described in Table 35.

The sketch in Figure 52 shows the bottom of the reactor about 50 feet above grade. This height was determined by a pressure balance since dense phase transfer of recycle solids is used and the pressure needed to elevate the solids is built-up in the reactor solids withdrawal standpipe. Thus the length of the standpipe, hence vessel elevation above grade, is set by the recycle solids requirements.

(6) Vessel Analytical Sketches

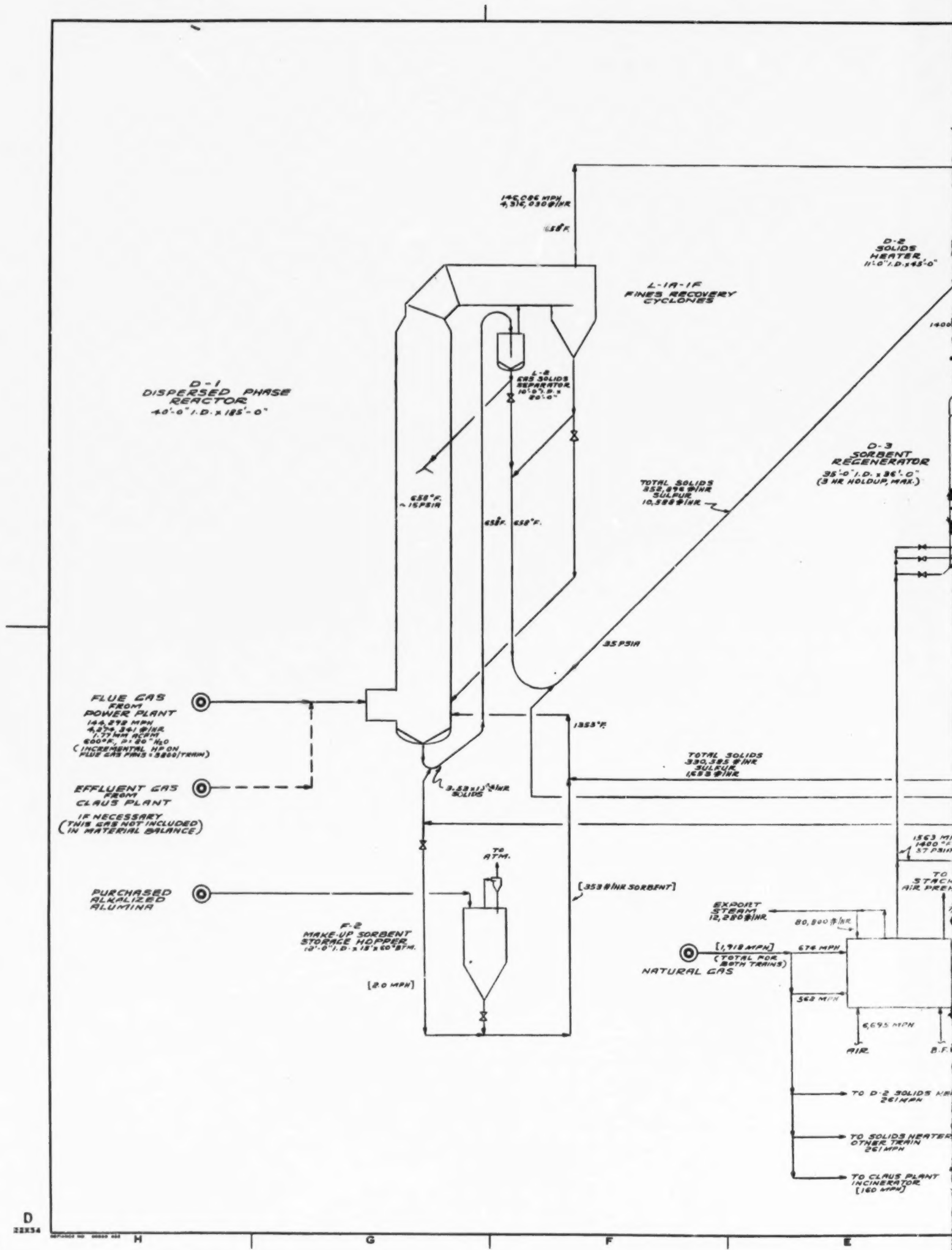
The process equipment sketches are included as Appendix Figures G-93 thru G-98.

b. Fluid Bed

(1) Fluid Bed Process Description: Flow Sheet P3198-D

The following process description is for the alkalized alumina process scheme shown on flow sheet P3198-D. The scheme is based on removing 90% of the SO_2 in the flue gases from a 1000 MW power plant burning a 3% sulfur coal.

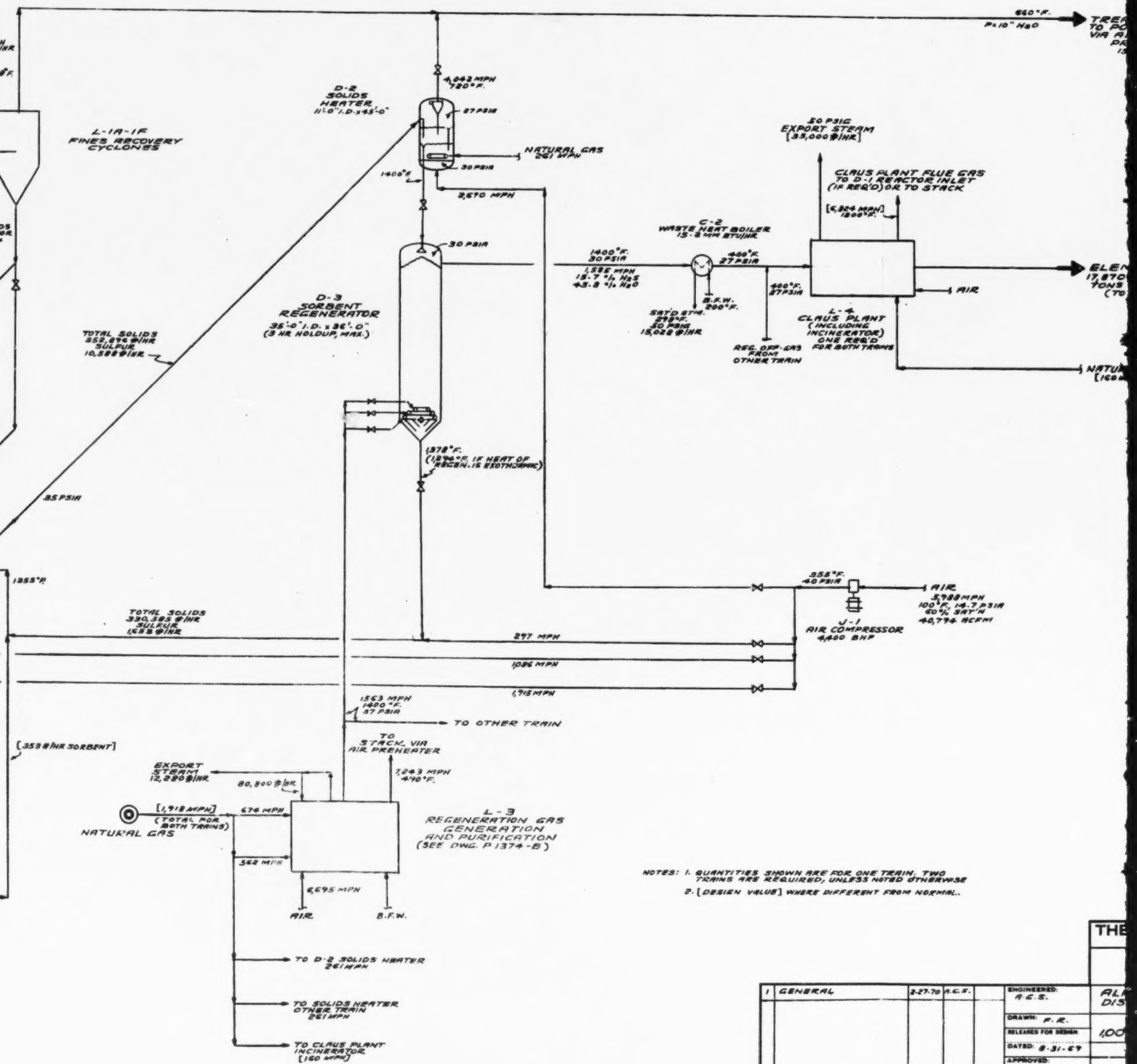
The equipment shown on this flow sheet is designed to handle 50% of the power plant effluent. The remaining 50% of the power plant effluent is fed to a second train of equipment identical to that shown on this flow sheet. In actual plant construction, however, the gas flow will not be split until after the flue gas booster fans. This will enable the use of a single inlet header, thereby decreasing duct construction costs. The same practice will be used for the sorber effluent gases with a single duct being provided at this point for the same reason as stated above. The flow sheet, therefore, schematically represents only the flows in one train



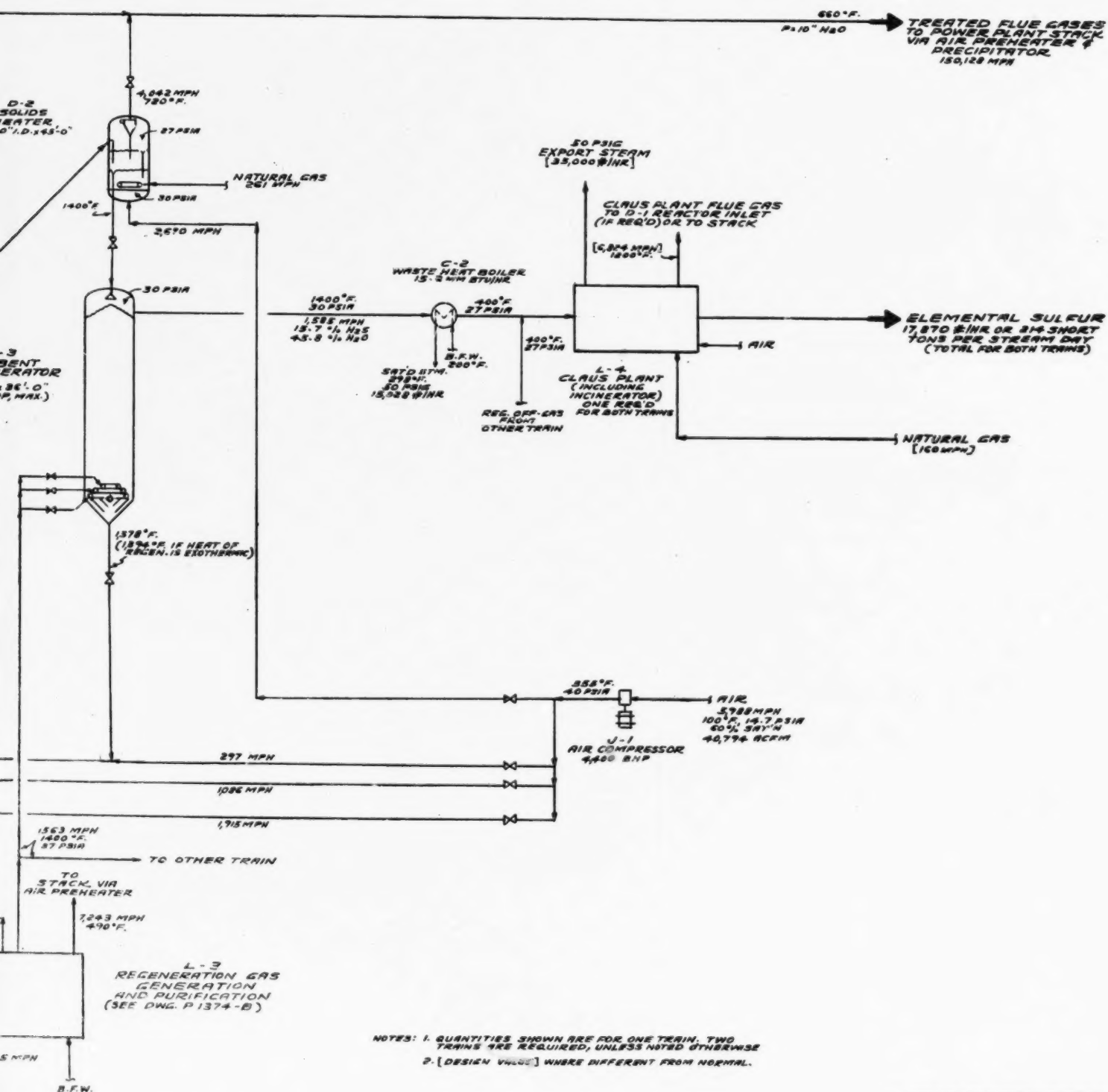
D
22X34

A

B



1	GENERAL	3-27-70	A.C.S.	ENGINEERED: A.C.S.	ALB DIS
				DRAWN: P.R.	100
				RELEASED FOR DESIGN	
				DATED: 8-31-69	
				APPROVED:	
NO.	DESCRIPTION	DATE	BY	APPROVED	ISSUED FOR CONSTRUCTION
REVISIONS					
					CLASS 5 (72)



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DESCRIPTION				DATE				BY				APPROVED				ISSUED FOR CONSTRUCTION			
REVISIONS																			

ALKALIZED ALUMINA PROCESS
DISPERSED PHASE FLOW SHEET

FOR
1,000 MW POWER PLANT FLUE GASES

6045 P3197-D

-222-

of equipment.

The SO₂-rich power plant effluent enters the flow sheet at 600°F and 10 in. H₂O after first passing through the power plant electrostatic precipitator. This gas is then compressed to 45 in. H₂O by the flue gas booster fan, J-1. The compression is required to overcome line losses and sorber pressure drop and enables the gas to be returned to the power plant circuit at the same pressure at which it was withdrawn. The compressed gases flow through the common inlet header and are then split into parallel feeds for each of the five fluid bed sorbers in the train. The gases pass through fluidized beds of alkalized alumina contained within these vessels where in SO₂ removal is effected.

The fluid bed sorbers, D-1 a thru e, are designed for 90% removal of SO₂. The number and height of these beds were determined by the CEGB-Blyth, and USBM-Albany sorption models, with appropriate safety factors. The SO₂-depleted effluent flue gas is then passed through internal cyclones to minimize sorbent losses. The exit gases from the sorbers enter the common exit gas header and are returned to the power plant circuit where they flow through the power plant air preheater for heat recovery before being discharged to the atmosphere via the stack.

The sulfur loaded sorbent leaves the sorbers via a solids overflow system and is then pneumatically conveyed to an intermediate feed hopper. This feed hopper, the gas-solids separator, L-1, serves three functions: first, it provides a common hopper for the solids discharge from each of the sorbers in the train; second, it provides a six minute holdup based on solids feed to the regeneration train, thus stabilizing possible fluctuations in flow; third, it provides enough elevation for a dense phase dipleg to build up sufficient

pressure (30 psia) to match that in the regeneration train.

The sulfur loaded sorbent leaves the gas-solids separator, L-1, through a dense phase fluidized standpipe and flows down 90 feet to a reverse loop where it is joined by a transport air line for pneumatic conveyance (@ 1 lb/cu ft loadings, throughput basis) to the regeneration train. The elevations of the regeneration train's solids heater and the gas-solids separator were set by a pressure balance around the pneumatic transport loops. A solids loading of two pounds per cubic foot was used in this calculation. This agrees with the slip factor of two which was estimated from the particle size distribution and theoretical settling velocities. The transport gas used in both loops is air at 35 psia.

The sulfur loaded solids enter the upper bed of the solids heater, D-3, at approximately 634°F. Two fluidized beds were used in this vessel to allow the 1400°F gaseous effluent from the lower bed to preheat the solids in the upper bed. This arrangement minimizes the natural gas and air requirements for the system by decreasing the duty required in the lower bed. The preheated solids leave the upper bed at 726°F via an overflow standpipe and are fed to the lower bed. The major part of the heating duty is supplied in this lower bed where the solids are heated by the direct combustion of natural gas and air. The solids leave the lower bed at the gas-solids equilibrium temperature, 1400°F, and exit via an overflow standpipe which feeds the sorbent regenerator, D-2.

The effluent gas from the upper bed of the heater mixes with the pneumatic transport air in the vapor space above the upper bed. These gases are then passed through an internal cyclone to separate the entrained solids from the gas stream. The mixed gases leave the vessel at 702°F and are let down by a valve from approximately 25 psia to 10 in. H₂O. The combined

heater effluent then flows to the main flue gas exit header for heat recovery and ultimate disposal through the power plant stack.

The sorbent leaves the solids heater at 1400°F and 30 psia and enters the fluid bed sorbent regenerator, D-2. In this vessel the sulfated alkalized alumina sorbent is regenerated with a reducing gas to desulfurize the sorbent from 7 weight percent sulfur to 2.6 weight percent. The sulfur-rich reducing gas effluent formed in the regenerator is passed through a cyclone to remove entrained solids and then sent to a Claus unit for sulfur recovery as elemental sulfur. A separate discussion of the Claus unit is given in section B.2.e, Part (3) of this report.

The regeneration gas is supplied to the regenerator from the steam-methane reformer, L-3. The reformer gas generation process flow sheet (P1374-B) and description are given in section B.2.e., Part (1) of this report. The regeneration gas at 1400°F and 25% excess over stoichiometric proportions enters the bottom of the vessel and passes through the fluidized sorbent bed, removing the sulfur from the sorbent. The products of the reduction reactions, based on a reformed natural gas feed are: sodium aluminate (NaAlO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS), sulfur dioxide (SO_2), elemental sulfur (S_2), and water. These gaseous products of the reactions leave overhead, while the sulfur depleted solids are withdrawn through a fluidized standpipe.

The solids leave the sorbent regenerator, D-2, at an average temperature of about 1400°F via five overflow standpipes. These standpipes are fluidized and are provided with control valves to regulate the flow in each line. The lines serve as the dense phase dipleg for a pneumatic air transport

system which carries the sorbent from the standpipes to the fluid bed sorbers, one line being used to feed each sorber. The regenerated sorbent then enters the sorbers and the cycle is completed.

Along with the major process loop of sorption, heating and regeneration, two other systems are shown on the flow sheet. These are the air and sorbent make-up systems. In the air system, air is compressed from atmospheric conditions to 40 psia by the air compressor, J-2. The air flow is then split into four streams: solids transport to the sorbers, solids transport to the gas-solids separator, solids transport to the solids heater and combustion air to the solids heater. The design temperature on the compressor effluent is 355°F. Thus the transport air modifies the temperature of the solids somewhat. For example, the regenerated solids are cooled from 1400°F to 1361°F by the transport air.

A make-up sorbent storage hopper, F-2, is provided to replace solids lost to the flue gas effluent through attrition. The vessel was designed to provide 1000 cubic feet of active storage capacity and thus be able to receive truck load quantities of purchased alkalized alumina sorbent. The solids discharge from the hopper is connected to the pneumatic transport system of a sorber feed line. Flows of make-up sorbent shown on the flow sheet are estimated since attrition data for this type of system are not available.

(2) Design Notes - Fluid Bed

Since at the time the fluid bed design was made the fluid bed test program (USBM-Albany) was just getting started and little experimental data were available, the process design is, of necessity, based mostly on literature correlations and various assumptions as to gas velocity, sulfur loadings, etc. The resulting design should provide a valid

preliminary basis for estimating the plant investment and calculating process economics, however, since any modifications resulting from differences in actual vs. assumed process variables will probably be small.

(a) Preliminary Process Calculations

1 - Minimum Fluidization Velocity

Initial investigation of the fluid bed system was undertaken using both empirical design methods and theoretical considerations. The range of the minimum fluidization velocities (U_{MF}), obtained from various correlations is shown in Table 36. With the exception of the Frantz correlation, all the calculated values for U_{MF} fall in the range 0.55 to 0.75 ft/sec. The average minimum fluidization value is 0.638 ft/sec plus or minus a 0.064 ft/sec standard deviation, if the Frantz correlation results are excluded. This exclusion is probably justified since the range of particle diameters studied by Frantz was well below the range of particle diameters encountered in the alkalized alumina system, and the resultant empirically derived "theoretical" equation developed by Frantz reflects this particle diameter range in the equation constant.

Values for the process variables used to define U_{MF} in the various correlations were obtained from published literature wherever possible or values were assumed when no information was available. Since equilibrium particle size distribution data from steady operation of fluidized beds were not available at the time this design was made, a size distribution had to be assumed. It was decided to use the particle size distribution reported in Table 4 of USBM-Bruceton Quarterly Report, June 30, 1968, for Grace #2 after the 3rd regeneration rather than that used in the dispersed phase design because the former has a slightly smaller amount of fines. The lesser

TABLE 36

MINIMUM FLUIDIZATION VELOCITIES AT 600°F AND 1 PSIG

<u>CORRELATION</u>	<u>REFERENCE</u>	<u>UMF (ft/sec)</u>
Ergun, S.	4	0.744
Leva, M.	1	0.559
Leva, M., et. al.	1	0.671
Miller, C. O. & Logivinuk, A. K.	1	0.622
Frantz, J. F.	3	1.117
Wen & Yu #1	2	0.600
Wen & Yu #2	2	0.634

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1. Leva, M., Fluidization, McGraw-Hill Book Company, Inc., New York, 1959. (pp. 63, 64 and 69).
 2. Kuni, D. and Levenspiel, O., Fluidization Engineering, John Wiley & Sons, Inc., New York, 1969. (p. 73).
 3. Frantz, J. F., Design for Fluidization, Chemical Engineering, September 17, 1962; Minimum Fluidization Velocities and Pressure Drop in Fluidized Beds, Chemical Engineering Progress Symposium Series, No. 62, Vol. 62, (p. 29).
 4. Ergun, S., Fluid Flow through Packed Columns, Chemical Engineering Progress, 48:89 (1952), (p. 81).

quantity of fines would be expected for fluid bed operation because of the lower gas velocity.

The weight mean particle diameter (D_p) was calculated from the cited particle size distribution and a value of 0.0359 inches or approximately 900 microns was obtained. For some of the correlations the particle shape factor and voidage at minimum fluidization were required and the assumed values of 1 and 0.4, respectively, were used. The bulk and particle densities of the sorbent were taken as 45 and 70 lbs/ft³ respectively, based on recent USBM data. These values give a fixed bed voidage of 0.357. Since a slight expansion occurs in the bed at incipient fluidization, the earlier assumption of a 0.4 voidage at U_{MF} is supported. The remainder of the variables used in the U_{MF} calculations are gas properties which have been fixed by the system. A typical calculation for U_{MF} is given in Appendix Table I-97.

Although the computed values agree fairly well, the actual minimum fluidization velocity should be verified in pilot plant or bench-scale work. The particulate matter used to determine the correlations mentioned earlier was for the most part non-vesicular and since the alkaliized alumina particles are very porous, it is possible that the correlations could give erroneous results.

2 - Fluid Bed Sorber Gas Velocity

To provide a basis for determining a reasonable operating range of superficial gas velocity in the fluid bed sorber, the terminal velocities of the maximum, minimum, and weight mean diameter particles were calculated. The maximum, mean, and minimum particle sizes of the sorbent cited previously (i.e., Grace #2 after 3 cycles) were determined and the terminal velocities, U_t , of these particles were calculated:

1. Maximum particle diameter, 0.081 in
(2057 microns):

$$U_t = 28.8 \text{ ft/sec}$$

2. Wt. mean particle diameter, 0.0359 in
(912 microns):

$$U_t = 13.6 \text{ ft/sec}$$

3. Minimum particle diameter, 0.008 in
(203 microns):

$$U_t = 2.2 \text{ ft/sec}$$

Although it would be preferable to run the fluid beds in a velocity range below the terminal velocity of the smallest size particles, this would be impractical due to the large volumes of gas being processed which would result in many large diameter reactors. For example, at a 2 ft/sec operating velocity, eleven 60' diameter beds are required. Therefore, it is desirable to use as high a gas velocity as practical and since no specific data are available, the design velocity has been arbitrarily set at 5 ft/sec. Under these conditions, the total cross-sectional area required (hence the number of beds) is greatly reduced while the gas velocity remains below the terminal velocity of the bulk of the particles, thereby keeping entrainment at a reasonable level. A range of superficial gas velocities should be evaluated in the pilot plant to determine the practical upper limit which could be used in a commercial design. Selection of the final design velocity would, of course, involve an optimization whereby reduced equipment cost resulting from higher gas velocities must be balanced against increases in bed height, pressure drop, and attrition losses.

3 - Comparison of Bed Heights Required for Fluid Bed Sorption - USBM-Albany vs. CEGB-Blyth Models

Once a superficial gas velocity is established, the bed height required to achieve the specified 90% SO₂ removal can be determined. This is a function of the kinetics of the system of which sorbent loading is an important variable. A kinetic model based on the Amundsen rate equation has been presented by the USBM-Albany¹ to represent the sorption reaction in fluidized beds of alkalized alumina. Using this model the sorbent inventory and therefore bed height were calculated for various assumed sulfur loadings.

The level of sulfur on the regenerated sorbent after it has been through enough sorption regeneration cycles to reach a equilibrium value was assumed to be 2.6% by weight. This value was based on regeneration data generated by USBM-Bruceton for various sorbents including Grace #1 and #2, Kaiser PR-15, and two USBM sorbents designated as 423X-4E and X-3F. The regeneration data reported naturally covered a wide range of temperature, initial sulfur loading, reducing gas composition and flow rate, and regeneration time. Since a commercial sorbent has not been developed, it was felt that for design purposes a satisfactory residual sulfur level could be determined from those test data that were obtained at approximately the design conditions. On this basis a concentration of 2.6% was selected as a reasonable design value since it was about mid-range of the pertinent test data. Other values in the range 2-3.5% could have been used instead but the process design and economics would not be changed appreciably from the present case.

The other sorbent and gas properties used were the same as those in the fixed bed study with the

¹ USBM-Albany, Progress Report, November 1968

exception of the reaction rate constant which was obtained from the USBM-Albany report cited previously. Table 37 presents a summary of the results obtained for various exit sorbent loadings.

The results given in Table 37 indicate that the theoretical settled bed heights required for sorption are small; i.e., the maximum predicted bed height is only 1.20 feet. However, this is a theoretical model and does not allow for the non-uniformity and physical non-ideality in the bed. The bed heights used in the actual sorber design were a static bed height of 2 feet and an expanded bed height of about 4 feet. This range of bed heights should provide sufficient contact time for sorption under actual operating conditions using a superficial gas velocity of 5 ft/sec.

The final sorber bed height is determined by the examination of many criteria. The sorption kinetics indicate a bed height of from 0.79-1.1 feet for a reactor 40 feet in diameter. These low bed heights are the result of the use of large diameter vessels which in turn are caused by the fact that large volumes of gas are being processed, and because the gas velocity must be kept at a reasonable level, say 2-5 feet per second. To provide good operability at 50% turndown (corresponding to off peak power operation), the lower value of gas velocity was set at about 4 to 5-fold above the minimum fluidization velocity. At the other end of the spectrum, gas velocities much above 5 feet/second cannot be tolerated due to the excessive entrainment they would incur. Attrition losses probably would increase also at higher velocities. Thus, the design velocity of 5 feet/second was chosen as a compromise between vessel and process requirements and, although an optimization of velocity could be made after sufficient data are available, it is unlikely

TABLE 37

SORBENT INVENTORY AND BED HEIGHT VERSUS EXIT SORBENT LOADING

USBM-ALBANY KINETIC MODEL-NOV. 1968 PROGRESS REPORT

SORBENT SULFUR LOADING @ EXIT, $\frac{1b\ S}{1b\ P}$	0.06	0.07	0.08
SORBENT INVENTORY, 1b	444,015	511,750	610,710
BED HEIGHT REQ'D, ft, @ GAS VELOCITY OF 5'/SEC:			
40' - DIAMETER*	0.785	0.905	1.08
50' - DIAMETER*	0.837	0.965	1.15
60' - DIAMETER*	0.872	1.01	1.20

* DIAMETER - No. of beds req'd.

40' - 10
50' - 6
60' - 4

that the final velocity would differ much from the value used. However, even at the operating velocity of 5 feet/second, large diameter vessels are required; e.g., 10 vessels @ 40 feet diameter, 6 vessels @ 50 feet diameter, etc. The selection of 40 feet as the vessel diameter was made to minimize the number of vessels used and yet not incur the operational problems of extremely large vessel diameters (40 feet diameter FCCU's are not uncommon in the petroleum industry).

With the vessel diameter, number of vessels, and bed heights required for sorption set, the pressure drop criterion must be tested. If a 30 inch H_2O pressure drop is allowed across the vessel (as in the fixed bed case) and the cyclone, distributor plate, and inlet losses are taken into account, the actual bed pressure drop becomes about 18.5 inches of H_2O . At this pressure drop the maximum allowable static bed height is 2.14 feet, well above the bed heights indicated by the kinetic models.

In order to improve gas distribution across the bed and thus operate under more stable conditions, and to provide a sufficient safety factor for the kinetic models, the static bed height was set at 2 feet. At this bed height and superficial gas velocity of 5 feet/second through the bed, a gas residence time of 0.4 seconds is obtained. This residence time compares favorably with that which is presently being studied in the USBM-Albany 4 inch fluid bed reactor.

In the area of fluid bed design, many empirical correlations and theoretical models have been presented in the literature. Due to the great variation which may be experienced in a particular fluidized system, however, the authors of these correlations recommend the physical verification of their work by pilot plant or bench-scale study.

The particular areas of study should be the verification of sorption kinetics at a 5 feet/second gas velocity over a range of sulfur loading on the sorbent, and the determination of the physical characteristics of fluidized alkalized alumina under process conditions. Some of the physical characteristics which should be determined before the final design of this type of system is undertaken are: bed height, pressure drop, bed expansion, transport disengaging height (T.D.H.), and the size and amount of solids carry-over above T.D.H. For the current studies however, it is believed that a design adequate for the present needs can be made based on available data and literature correlations. Necessary adjustments can be made as required when more experimental data become available.

(b) Vessel Design

In the fluid bed sorption process, all of the major process vessels, namely the sorbers, regenerators, and heaters, are designed as fluid bed equipment. The sorbers and regenerators are fluid beds by definition in the study, so as to compare this type of operation to the fixed and dispersed phase bed types studied separately. The solids heaters became fluid beds through the optimization of equipment design and process conditions and their selection as such bears no relationship to the definition of the type of sorption used.

1 - Sorber

The fluid bed sorber was designed using various empirical and/or theoretical correlations; the correlation used for each specific section of the vessel has been noted and referenced. For the 1000 megawatt power plant design basis, ten 40 foot diameter fluid bed sorbers were used, giving a superficial gas velocity at full load of approximately 5 feet/second. As noted previously, the static bed height will be 2 feet. Since no bed expansion data are presently available, the

expanded bed height was assumed to be 4 feet, i.e., a 100% expansion. The solids dust loading was set by means of the particle size distribution given in a USBM-Bruceton Quarterly Report¹* and the catalyst entrainment correlation of Zenz and Weil². With a solids dust loading set, the cyclone pressure drop was calculated for a 60 feet/ second inlet velocity based on an internal MWK correlation. The inlet gas distributor was designed as a baffle type to minimize the height required for the inlet. The sizing and pressure drop calculations for this distributor were done using MWK correlations. The catalyst support and distributor plate was sized to give the optimum hole spacing at the maximum pressure drop using the correlation recommended by Zenz³. Once the inlet, distributor and cyclone pressure drops were calculated, a check was made to insure that the actual total pressure drop agreed with the assumed total pressure drop of 30 inches H₂O.

The cyclone size and dimensions were approximated from the typical proportions given in Perry's⁴. All cyclone dimensions given are comparable to this reference with the exception of the top cylindrical section. Because of the extreme size of this section a check will be made through cyclone vendors to determine whether it is applicable to this system or not. Alternatively, it may be desirable to use several smaller cyclones in parallel as in FCCU practice.⁺ In any case all cyclone dimensions will be verified by a vendor before an estimate of this system is made. The cyclone dip-leg was sized using an MWK correlation.

The sorbent withdrawal line from the reactor is a dense phase, 30 lb/ft³, fluidized line which feeds into a dilute phase, 1-2 lb/ft³, solids transport line. The sizes of these lines were determined by an internal MWK correlation as was the solids feed line. The solids inlet

* Numbers refer to references at the end of this section.

+ Subsequently it was decided to use smaller cyclones in parallel in the final design.

nozzle was sized to give a velocity of approximately one half of the transport velocity and was elevated 20 feet above the top of the bed to provide sufficient room for the solids to disengage from the transport gas. A detailed vessel sketch and notes are given in Figure I-99 as drawings AA-FB-3-A1 through A-4.

2 - Regenerator

The regeneration reactor for this system is a fluid bed operating at 1400°F and an exit gas pressure of 15 psig. A regeneration temperature of 1400°F was selected for the reasons given previously in this report under section B,2,a.(2)(b)2- Dispersed Phase Vessel Design-Solids Heater; viz., at 1400°F better reaction kinetics and a more economical solids heater design are obtained. For the design purposes the CEGB-Blyth kinetic regeneration model was used along with a 50% safety factor on residence time. This 50% safety factor, plus the added safety factor obtained by using a sorbent with higher regeneration rate characteristics, should provide a regenerator design capable of handling minor temperature variations and varying intersititial sulfur loading without adversely affecting sorbent regeneration. Based on respective inlet and outlet sorbent loadings of 7 and 2.6 weight percent sulfur, a solids residence time of 30 minutes was obtained.

Two regeneration sections comprising a regenerator and heater, were used in the design with each regenerator section handling the solids flow from five sorbers. This arrangement minimizes both vessel sizes and length of transport lines since the regenerator sections can be located symmetrically on the plot plan.

The regenerator vessel was sized using the following bases: 1) a superficial gas velocity of 2 feet/second, and 2) a sorbent inventory of 84,000 lbs (30 minute holdup). The gas velocity in the vessel was set at 2 feet/second to allow for 1 foot/second superficial velocity operation

during non-peak load (50% flow). At this latter velocity, the flow is approximately double the theoretical minimum fluidization velocity. Under these design conditions the vessel diameter was found to be 12 feet and the static bed height for normal operation was calculated to be 16-1/2 feet. In order to provide for uncertainties in the regeneration kinetics (e.g., effect of back-mixing of solids in the fluid bed), a 50% safety factor based on sorbent inventory is provided, so that a total bed height of 25 feet is obtained.

The gas residence time obtained by using a 16-1/2 foot bed at 2 feet/second is approximately 8 seconds. This value corresponds to a space velocity of 950 hr⁻¹. Space velocities in the range of 1000 hr⁻¹ have been run successfully in the Bruceton thin bed tests but these values should be confirmed in the Albany fluid bed regeneration tests.

For the actual vessel design, e.g., cyclone, gas distributor etc., refer to section (b) 5.

3 - Fluid Bed Heater

The solids heater used in the fluid bed sorption system is the same type which was used in the dispersed phase system. It is composed of two fluidized beds arranged in series in a single vessel. In the lower bed natural gas is burned with air to heat the sulfur laden solids to the 1400°F regeneration temperature. The bed height in the lower bed was set at 10 feet to satisfy combustion requirements. Based on the fact that the exit solids and gas temperature are in equilibrium, the combustion products leave the first stage at 1400°F and pass through the upper bed where they preheat the solids from 634°F to the equilibrium gas-solids temperature of the upper bed which is 726°F. The gas temperature drops to 702°F at the vessel exit as a result of mixing the transport air with the heater gas above the top bed.

The solids heater was sized on the basis of a 5 feet/second superficial gas velocity for the effluent of the lower stage. Using this criterion, a vessel diameter of 9'-0" was obtained. The bed height for the lower bed was specified at 10'-0" and a 5'-0" spacing was left between the upper and lower beds to de-entrain the bulk of the solids carried out of the lower bed. Since the upper bed is a gas-solids heat transfer stage with no combustion occurring, an expanded bed height of one foot was provided (based on the dispersed phase bed calculations, this should provide more than sufficient height for heat transfer). The minimum fluidization velocities were then calculated for each of the heater sections and compared to the actual superficial velocities being run in these sections. In all cases the actual velocities exceeded the minimum fluidization velocity by at least a factor of 4, thus providing a safety factor of 100% during non-peak gas flow.

As in the case of the regenerator the various correlations and parameters used in the vessel design and equipment specification are given in section (b) 5.

4 - Process and Mechanical Considerations Regenerator Train

The major process consideration for setting operating pressure in the regeneration train was the overhead composition and temperature of the fluid bed regenerator. The pressure drop through the Claus plant including any pretreatment equipment that might be required, sets the pressure of the regenerator off-gas. Two methods for increasing the regenerator effluent pressure were considered: 1) provide a compressor for the regenerator effluent, or 2), increase the inlet pressure in the regenerator. The first alternative would require costly materials of construction for the off-gas compressor in that the regen-

erator effluent contains a high quantity of sulfur compounds at 1400°F. Larger sized vessels for the solids heater and regenerator also would be required at the lower pressure. If not required by process considerations, therefore, a low pressure (0 psig) regeneration system with compression of the off-gas has little if any advantage over a high pressure (15 psig) system. On the other hand, the second proposal has some significant advantages in that, by increasing the operating pressure of the regenerator, the gas is compressed up-stream of the regenerator thus decreasing the vessel diameter and the line sizes to and from the regenerator. Another beneficial effect derived from increasing regenerator operating pressure is the reduction in size of the solids heater since this vessel is run at nominally the same pressure as the regenerator due to the solids overflow feed system. Therefore, the higher pressure alternative was used in the design and the regenerator effluent pressure was set at 30 psia.

The solids feed system for the regenerator train is a dense phase standpipe arrangement with the solids overflow from the beds used as the standpipe feed.

The vessel internals for the regeneration train distributors, cyclones, grids, etc., were sized using empirical and theoretical correlations.

Vessel diameters, bed heights, temperatures and pressures were set by process considerations (see specific vessel section for details of the above). Once these parameters were specified the transport disengaging heights, TDH, were calculated using the correlations of Zenz and Weil². The solids loading at TDH was then calculated using the particle size distribution given in a USBM quarterly report¹, the superficial gas velocity for each

vessel, and the catalyst entrainment correlation proposed by Zenz and Weil². With the solids dust loadings set, the cyclone pressure drops were calculated and cyclone selection was made using vendor supplied data.

Two types of gas inlet distributors were specified for the regeneration train: a baffle type for the regenerator, and slotted pipe types for the solids heater and solids cooler. The sizing and pressure drops for these distributors were done using MWK correlations. The catalyst support and distributor plate for each vessel were sized to give the optimum hole spacing at the maximum pressure drop using the correlation recommended by Zenz³. The solids inlet line for the solids heater was sized to provide a velocity equal to half of the transport velocity and thus decrease the penetration of the solids into the bed. Slots are provided in this line to allow at least a partial gas-solids separation before impingement on the bed, which further decreases solids penetration. Solids withdrawal from the beds in the regeneration train is handled by dense phase standpipes with cone top feeders to capture the overflow solids. Three concentric pipe rings are used to feed natural gas to the bottom bed of the solids heater. These rings were designed to provide uniform heat transfer by maximizing the gas distribution in the bed.

The vessel sketches and design data for these vessels, the regenerator and solids heater, are shown in Figures I-100 and I-101, respectively.

5 - Plant Layout

A preliminary plant layout study was undertaken to determine an optimum vessel configuration so as to minimize both the amount of the large diameter ducting required, and the plot size and field fabrication problems associated with this ducting. Consequently, seven different

layouts were made and evaluated. The study results indicated that there was little difference between the configuration in terms of total cost; the maximum cost was about 5% higher than the minimum cost, based on the approximate estimating techniques used for this study. The case which was finally selected had an estimated cost for materials and construction that was midway between the highest and lowest but gave the minimum plot area and simplest layout. A plot plan showing this layout is presented as Figure 54. Since all the vessels are at nominally the same pressure, they are stacked to allow gravity feeding between vessels. A tentative layout of the proposed plant, Figure 55, shows the elevations required to obtain this type of solids feed system.

6 - Solids Transport System

The transfer of sorbent particles between the reactors and regeneration train is done pneumatically, using dilute phase gas-solid mixtures. However, because of the difference in operating pressure between the reactor and regenerator train (i.e., 15 psia vs. 30 psia respectively), the reactor exit solids cannot be fed directly into the solids heater without some means of increasing the pressure in the solids feed line. This is done by use of an intermediate feed hopper sufficiently elevated so that the necessary pressure buildup is obtained in the dense phase leg, thus providing the solids driving force for the pneumatic elevation of the sorbent to the solids heater.

The line sizes and transport gas requirements have been calculated based on a solids loading of one pound per cubic foot for the dilute phase lines, and 30 pounds per cubic foot for the dense phase standpipes. However, for the pressure drop calculations a slip factor of two was used, this value having been estimated from the particle size

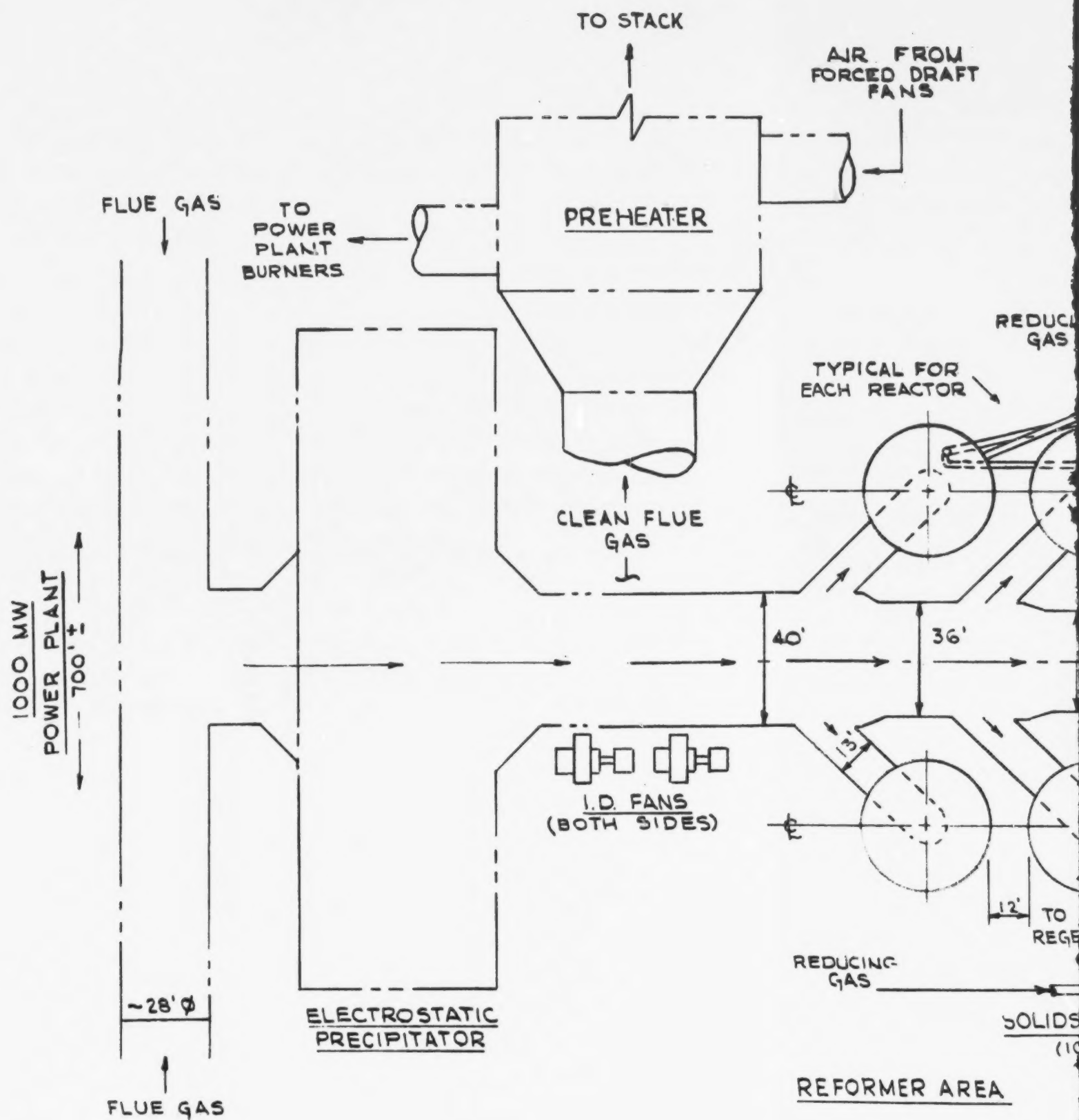


FIGURE 54
FLUID BED SORPTION EQUIPMENT
(PLAN VIEW)

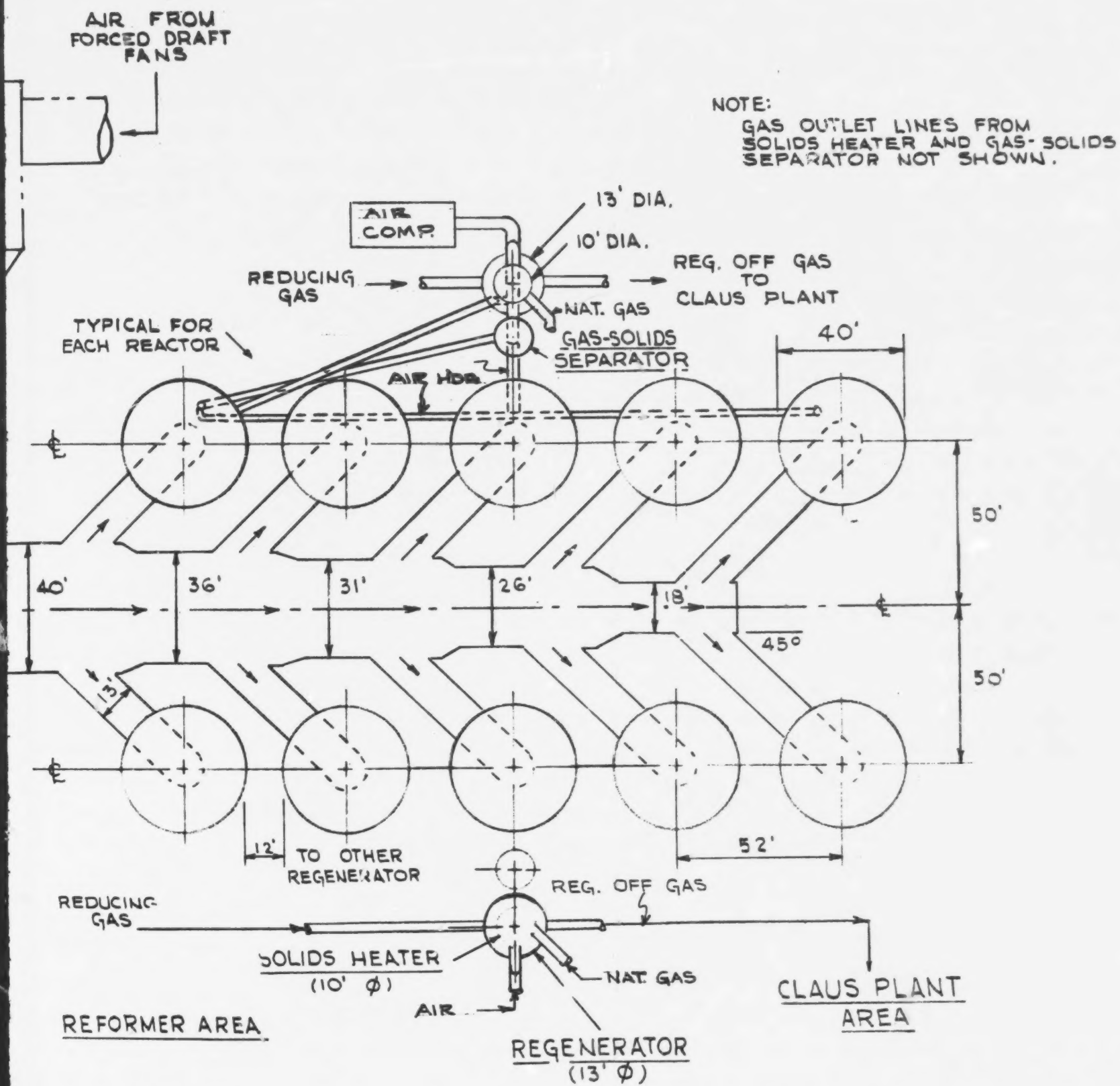
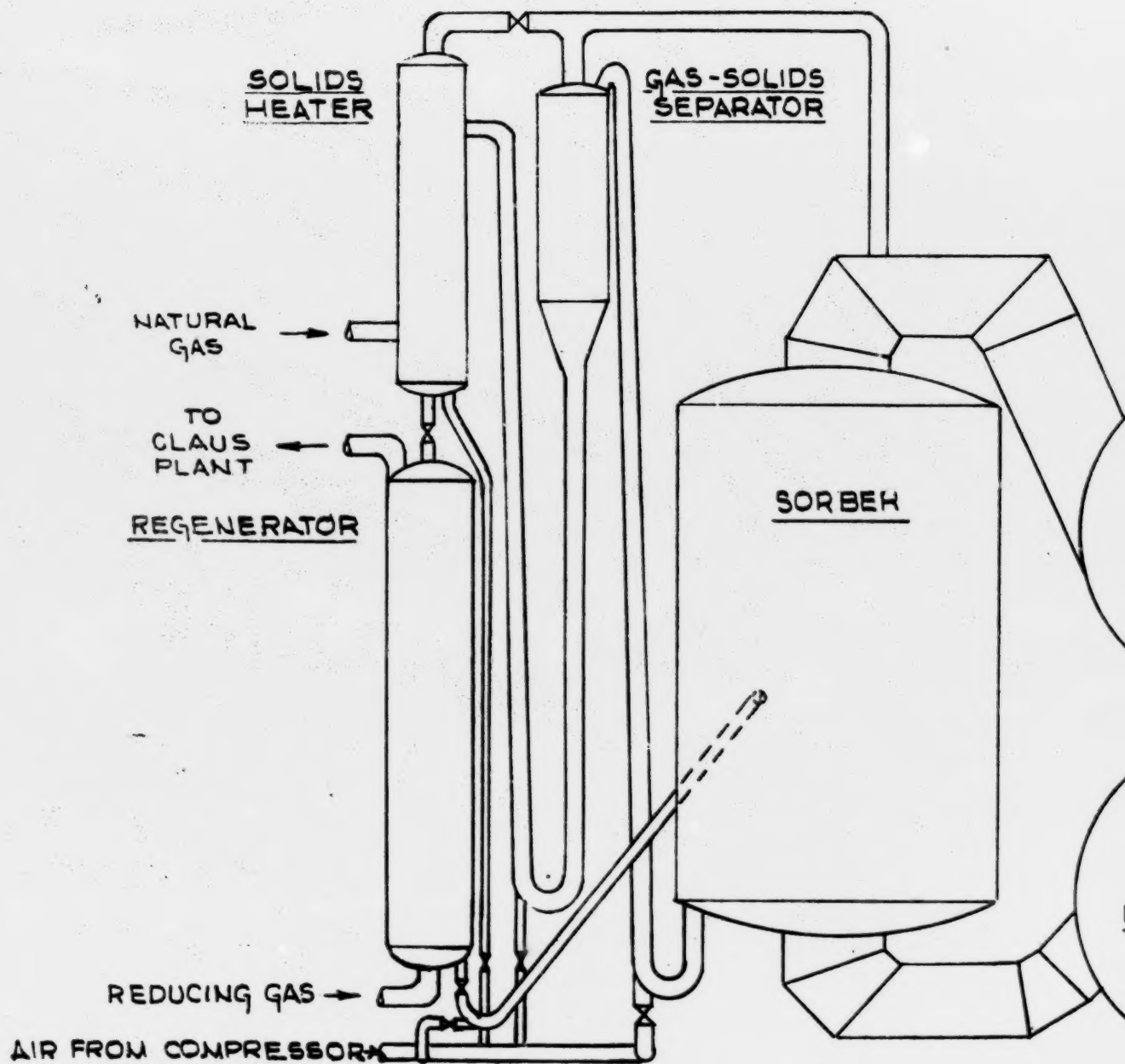


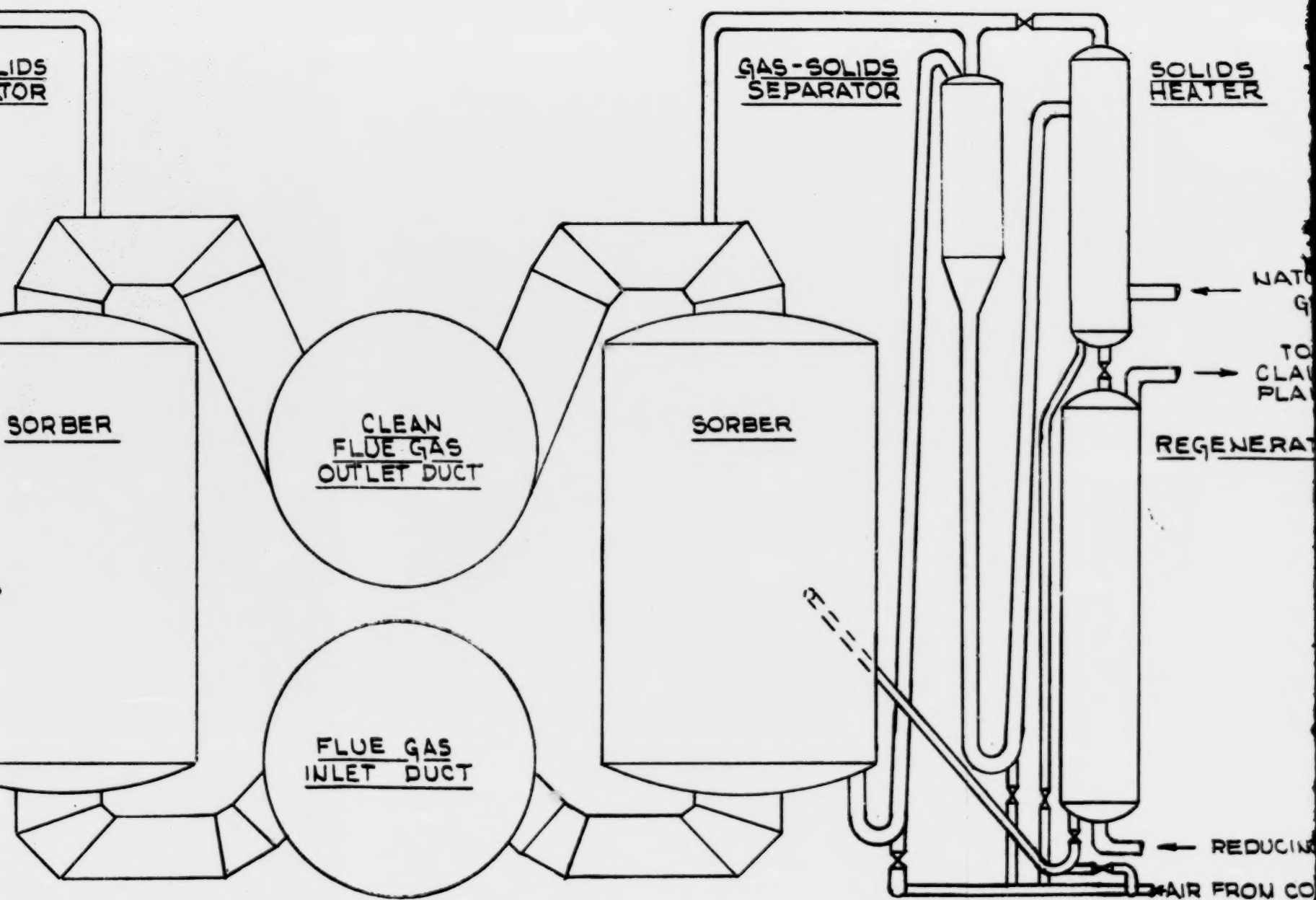
FIGURE 54
SORPTION EQUIPMENT LAYOUT
(PLAN VIEW)

B



FLUID BED SOR

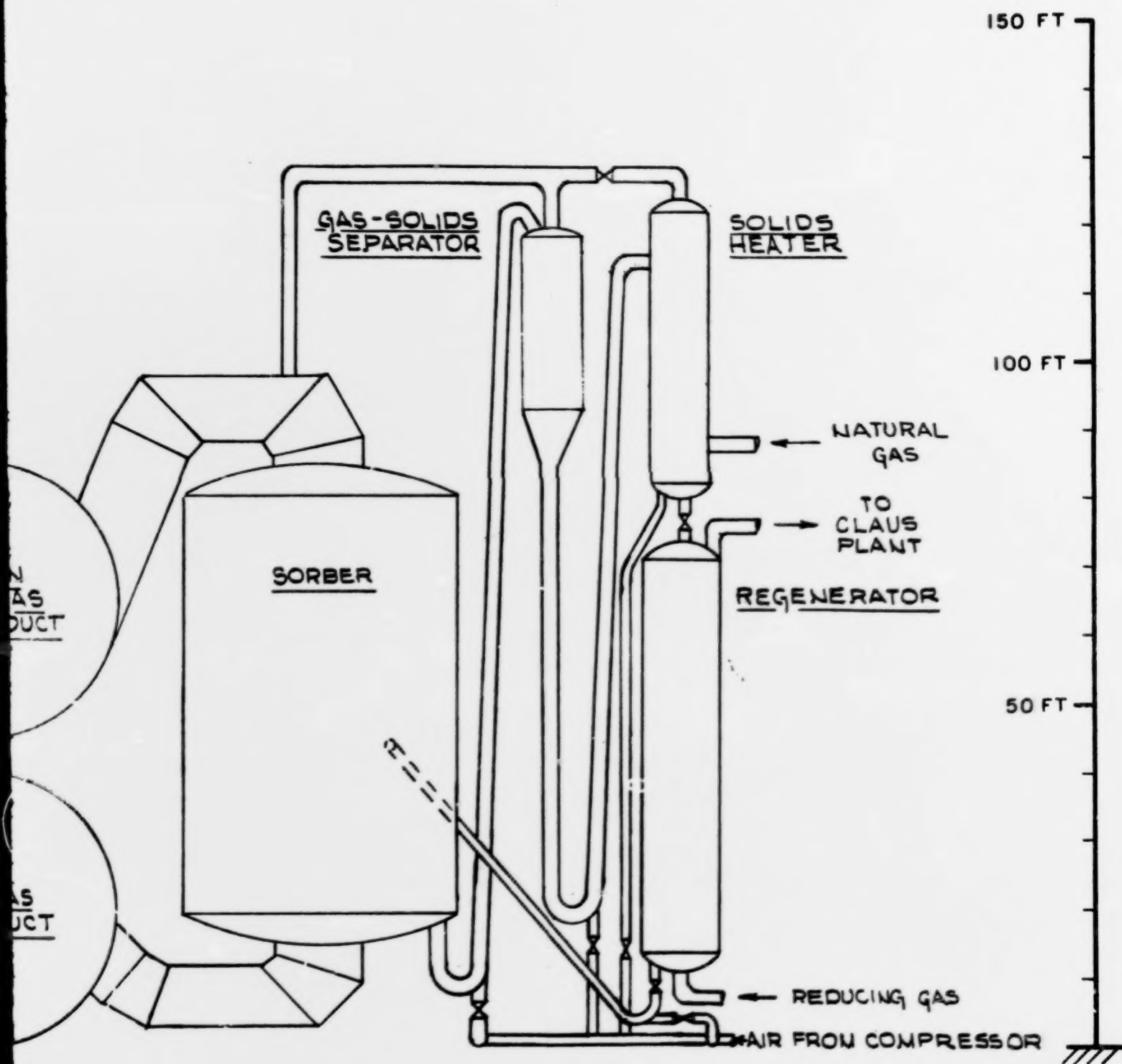
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NOTE:
STRUCTURAL STEEL NOT SHOWN.

FIGURE 55
FLUID BED SORPTION EQUIPMENT LAYOUT
(ELEVATION)

B



NOTE:
STRUCTURAL STEEL NOT SHOWN.

55
EQUIPMENT LAYOUT
(ON)

0

distribution and theoretical settling velocities. Compressed air at 35 psia was used as the transport gas in the pressure drop calculation and the intermediate feed hopper elevation was calculated to be 115 feet.

7 - Gas-Solids Separator

The intermediate feed hopper, mentioned in the previous section, was designated as the gas-solids separator. This vessel has the dual function of providing a gas-solids disengaging region for the dilute phase risers and providing a six minute surge capacity, based on solid flow, to insure a fairly constant head on the dense phase standpipe. The vessel diameter was set at 9'-0" by assuming an L/D ratio of approximately 1. A cyclone was provided to minimize solids losses. The vessel is fed by risers from each of the five sorbers in the train. As in the case of the fluid bed designs, these inlet lines are designed for a reduced velocity and are fitted with slotted ends. The vessel is provided with a steep cone bottom to insure drainage into the standpipe at all times. This vessel is shown as Figure I-102.

8 - Air System

Compressed air at 35 psia is provided as combustion air to the solids heater and as a transport medium for the solids. A single air compressor per train is furnished for this service. The compressor discharge is split via appropriate controls into the four separate streams required.

REFERENCES

1. USBM-Bruceton Quarterly Report, June 30, 1968, Table 4.
2. Zenz, F. A. & Weil, N. A., A Theoretical-Empirical Approach to the Mechanism of Particle Entrainment from Fluidized Beds, AIChE Journal, December 1958, Vol. 4, No. 4, pp. 472-479.
3. Zenz, F. A., Bubble Formation and Grid Design, Tripartite Chemical Engineering Conference, Symposium on Fluidization II, Session 32, September 25, 1968 (Montreal)
4. Perry, R. H., et. al., Chemical Engineer's Handbook, McGraw-Hill Book Company, N. Y. 1963, pp. 20-69.

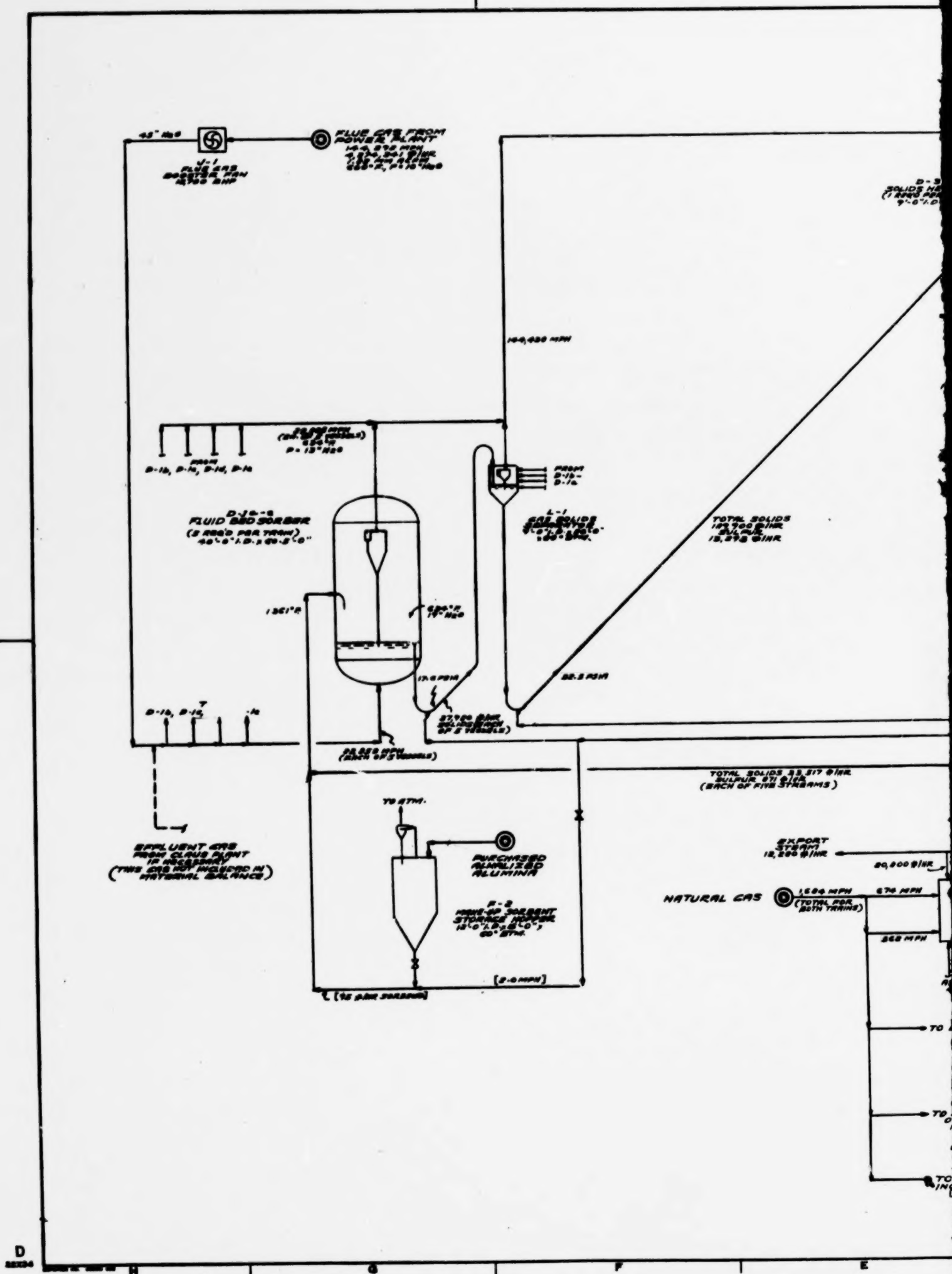
c. Fixed Bed

(1) Fixed Bed Process Description:
Flow Sheet P3196-D

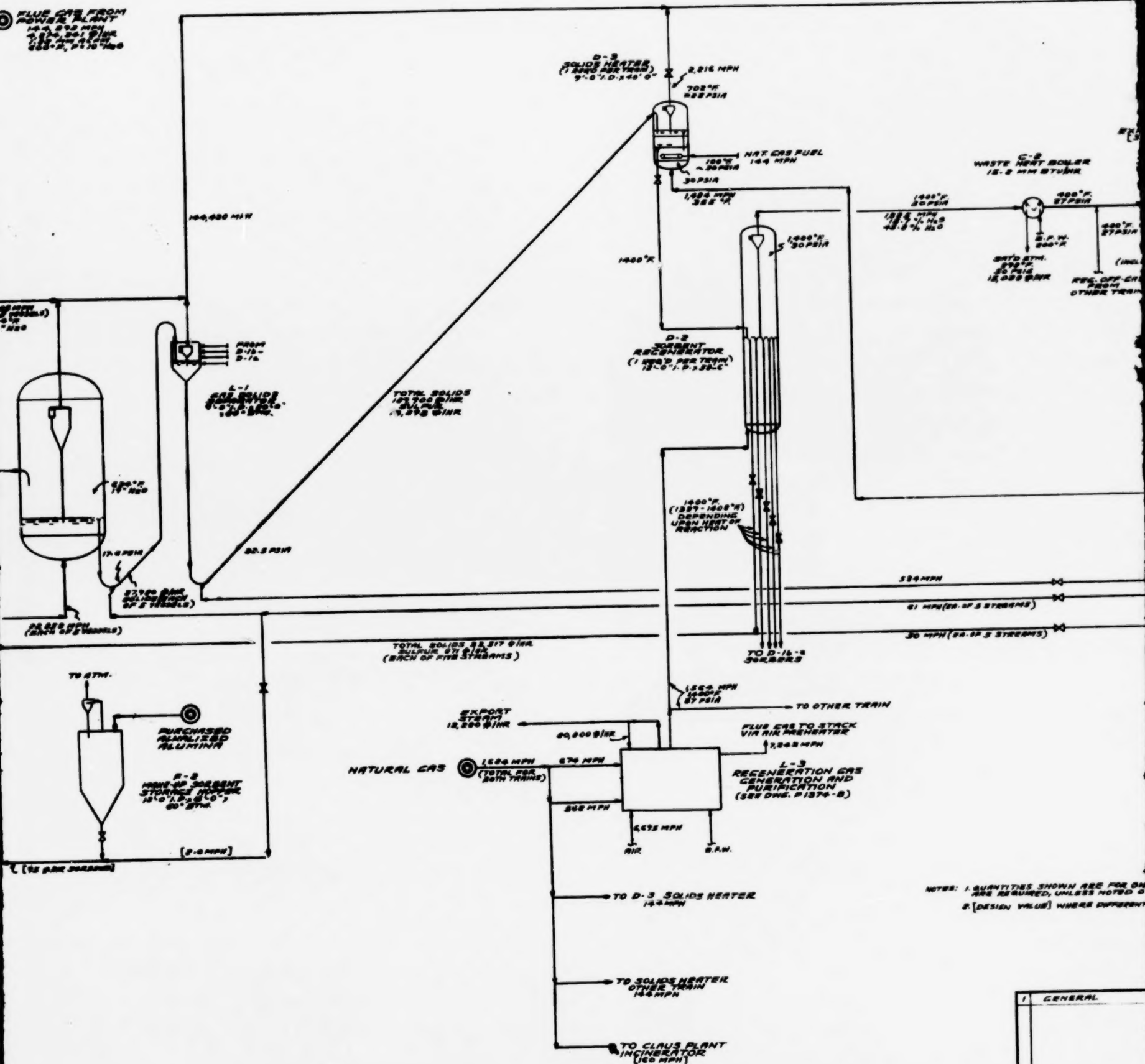
The SO₂-rich flue gas from a 1000 megawatt power plant burning a 3% sulfur coal enters the flow sheet after leaving the power plant's precipitator at 600°F, as stream 1. Stream 1 is compressed by the flue gas booster fan, J-1, from 10 inches of water to 45 inches of water to overcome the line losses and bed pressure drop in the SO₂ removal scheme, calculated to be 35 inches of water; thus the flue gas is returned to the power plant circuit at the same pressure at which it was withdrawn. The compressed gas then enters a header, common to the four fixed bed sorbers, D-1 thru 4. During steady state operation, two of the four sorbers will serve to remove SO₂ from the flue gas, while the remaining two sorbers will be in the regeneration, heating or cooling cycle. A sorber by-pass line to the power plant stack via the air preheater is also provided on the header. This line is designed to accept 50% of the stream 1 flow should maintenance require one of the sorbers to be shut down temporarily.

The stream 1 flow from the header is split and fed to each of the two reactors in which sorption is occurring (in the case shown on the flow sheet sorbers D1 and D2) as streams 1-A & 1-B. Each sorber is composed of 84 annular sorbent beds of alkalized alumina enclosed in a rectangular chamber. The beds are 3'-7" O.D. by 2'-4" I.D. by 22'-0" high, giving a bed thickness of ~7" and a bed pressure drop of 30 in. H₂O, and are described in the design notes.

The flue gas from stream 1 flows into the rectangular sorber chamber then through the annular sorbent beds where SO₂ is removed from the gas stream. The clean flue gas then flows up the center cylinder, formed by the annulus, to a

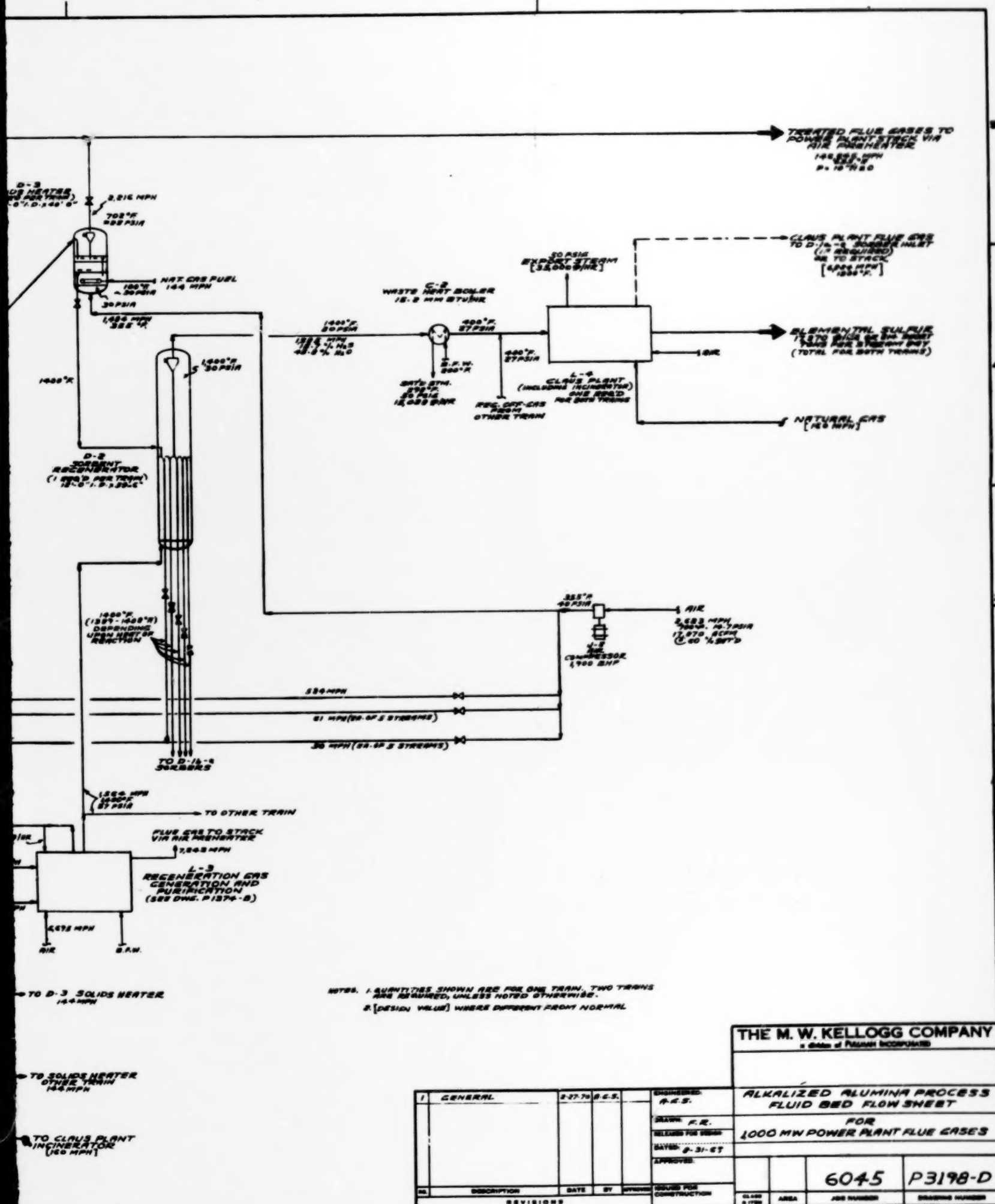


FLUE GAS FROM
POWER PLANT
14-4-89 200 MPH
7-25-89 201 210K
7-25-89 200 210K
255-2, P 10-100



NOTES: 1. QUANTITIES SHOWN ARE FOR ONE
ARE REQUIRED, UNLESS NOTED OTHERWISE
2. [DESIGN VALUE] WHERE DIFFERENT

GENERAL	
NO.	DESCRIPTION



common sorber exit gas chamber and out of the sorber to the effluent flue gas header, stream 2. The clean flue gases flow through this header and combine with the sorber heating or cooling gas from a third sorber. A side stream, stream 4, is withdrawn from these mixed gases for use as a heating or cooling medium for the sorbent beds. The remainder of these mixed gases, stream 3, leaves the process area and flows to the power plant air preheater for heat recovery before being discharged through the stack.

Because the process utilizes fixed bed sorption and regeneration, the operation is on a batch rather than a continuous basis. The cycle time for this process was set by allowing two hours as the time required for the regeneration step (and one hour each for heating and cooling the beds to and from the regeneration temperature of 1200°F. Thus a total heating-regenerating cooling time of four hours is obtained. Based on the above, plus a four hour sorption time, a complete cycling of the sorbers is made in eight hours. Four sorbers and one hour heating and cooling time were chosen to allow major process equipment (such as the recycle flue gas blower, J-2, the regeneration gas generation and purification sections, and the Claus-gas purification section) to operate on a continuous basis.

As mentioned earlier, the sorbent beds must be preheated from the 600°F sorption temperature to the 1200°F level required for the regeneration reaction. Recycled flue gas from the sorber exit header is used as the heating medium for this purpose, and is taken off as a side stream from the effluent flue gas heater, stream 2. This side stream of recycle flue gas, stream 4, is compressed from 10 in. H₂O to 25 in. H₂O, by the recycle flue gas blower, J-2, to overcome line losses and bed pressure drop, which are smaller

than for the flue gas circuit because of the smaller gas flow. The recycle gas at 602°F is then passed through the convection section of a natural gas fired furnace where the furnace's combustion products are mixed with the recycle gas. This furnace, the recycle flue gas heater, B-1, was designed to give an effluent flue gas temperature of 1225°F, when using 10% excess air. Two blowers, the air blower, J-3, and the pilot air blower, J-4, provide the air required for combustion in this furnace. Both blowers are designed to provide a positive pressure of 25 in. H₂O, which is sufficient to move the heating gas through the fixed sorbent beds.

The pilot air blower, J-4, serves the function of providing combustion air, stream 5-A, during the cooling cycle when no process flow is required through the furnace. The combustion products from the pilot burner serve to maintain the operation temperature in the furnace, thus preventing thermal cycling in the furnace during the no-flow condition. The effluent from the pilot burner is fed directly to the stack through its own exhaust duct which ties into the clean flue gas duct, stream 3, downstream of the sorbers.

The recycle heating gas effluent from the furnace, stream 7, enters the common sorber inlet duct, stream 1-D, and flows through the sorbent beds, preheating them to 1200°F for regeneration. Heat transfer in the fixed bed is very rapid with the temperature profile in the bed appearing as a sharp wave-front. Because of this, the exit gas temperature is 600°F, the initial bed temperature, for almost the entire heating cycle. It is only during the end of the cycle that the wave-front begins to break through causing an increase in the exit gas temperature. The average bed exit temperature is 625°F, whereas the final bed exit temperature is approximately 1200°F. The spent heating gas then leaves the sorber via the common sorber effluent duct, stream 2-D, and flows into stream 2 for disposal to the stack.

The cooling cycle is essentially the same as the heating cycle; i.e., clean flue gas from stream 2 is recycled to the sorbers to cool the beds from 1200°F to the sorption temperature. There are, however, two differences in this cycle; first, the recycle flue gas heater, B-1, is by-passed; second, the bed exit temperature for the cooling gas is 1200°F for the greater part of the cycle. Due to the latter difference the average effluent gas temperature is increased which means that the recycled gas cannot cool the beds down to the sorption temperature of 600°F, but rather to the mix temperature of the gas in the effluent header, 675°F. To compensate for this, the gas flow rate is increased slightly thus causing an earlier break-through. Once break-through occurs, the effluent gas temperature drops off sharply, giving a mix temperature in the effluent gas header of approximately 600°F. Therefore, during the remainder of the cycle gas inlet cooling gas to the sorber is at the desired temperature. This cooler gas removes further heat by forming a second wave-front in the bed. This wave front precools the front section of the bed at 600°F for sorption and propagates itself as further 600°F gas is passed through the bed. Even if the entire bed has not been cooled to 600°F at the end of the cooling cycle, the introduction of 600°F flue gas for sorption will continue to cool the sorbent by extending the cooling wave-front ahead of the reaction zone.

The last operation cycle is that of regeneration. The sulfated alkalized alumina is regenerated with a reducing gas to desulfurize the alumina and form a sulfur-rich gas which can be fed to a Claus unit for sulfur recovery as elemental sulfur. On the present flow sheet, a 1200°F reformed natural gas, containing 10% CO, was used as the reducing agent. The regeneration gas generation and purification stages are shown on a separate flow sheet, P1374-B, section B.2.e. part (1) of this report. Similarly, the regeneration gas effluent from

the sorbers has to be pre-treated prior to entering the Claus unit; the Claus-gas purification stage is also shown on a separate flow sheet, Pl375-B, and discussed in section B.2.e. part (2) of this report.

The assumed regeneration gas, containing a 25% excess over stoichiometric proportions, flows as stream 8 to the common sorber inlet duct, stream 1-C, at 1200°F. Leaving the inlet duct, the gas passes into the sorber and through the annular sorbent beds to remove the sulfur from the sorbent. The products of this reduction reaction, based on a natural gas reformat, are: sodium aluminate (NaAlO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS), sulfur dioxide (SO_2), elemental sulfur (S_2), and water. This sulfur-rich gas flows out of the common sorber exit duct, stream 2-C, to the regeneration gas effluent header, stream 9. This header feeds the Claus gas purification stage where the gas is pre-treated (H_2O removal, etc.) and sent to the Claus unit for sulfur recovery as elemental sulfur.

The high process temperatures encountered in the large ducts require water-cooled closure rings (i.e., valve seats) to minimize thermal stresses in the duct walls. To avoid scale formation in the rings, treated cooling water is required. This water will be made available from off-site facilities.

It should be noted that the sorber operation shown on the flow sheet corresponds to the first set of conditions given in Table 38 which outlines the proposed operation schedule for each of the four sorbers. The material balance given in Table 39 shows the process flows for the major process streams, also for the first set of conditions in Table 38. To show the changes in stream flow which occur during a cooling cycle, Table 40 was provided as an alternate to Table 39. Table 40 shows only those flows which would be affected by the cooling cycle; all other flows are the same during both the heating and cooling cycles.

TABLE 38
SORBER OPERATIONS SCHEDULE

TIME (HRS)	<u>SORBER</u>			
	D-1	D-2	D-3	D-4
0	S	S	R	H
1	S	S	C	R
2	H	S	S	R
3	R	S	S	C
4	R	H	S	S
5	C	R	S	S
6	S	R	H	S
7	S	C	R	S
8	S	S	R	H

NOTES: S denotes a train which is sorbing SO₂
R denotes a train which is being regenerated
H denotes a train which is being heated
C denotes a train which is being cooled
0-7 represents one complete cycle; 8 is identical to 0
and is the start of another cycle

TABLE 39

HEATING CYCLE MATERIAL BALANCE

STREAM NO.		1 (INLET FLUE GAS FROM POWER PLANT)		1-A (FLUE GAS INLET TO SORBER D-1)		1-B (FLUE GAS INLET TO SORBER D-1)	
COMPOSITION	M.W.	LB/HR	MPH	LB/HR	MPH	LB/HR	MPH
CO	28.011						
CO ₂	44.010	1,755,024	39,877.84	877,512	19,938.92	877,512	19,938.92
COS	60.075						
H ₂	2.016						
H ₂ O	18.015	423,792	23,524.42	211,896	11,762.21	211,896	11,762.21
H ₂ S	34.080						
N ₂	28.013	6,024,234	215,048.30	3,012,117	107,524.15	3,012,117	107,524.15
O ₂	31.999	304,411	9,513.14	152,206	4,756.57	152,206	4,756.57
S ₂	64.128						
SO ₂	64.063	39,674	619.30	19,837	309.65	19,837	309.65
CH ₄	16.043						
TOTAL		8,547,135	288,583.00	4,273,568	144,291.50	4,273,568	144,291.50
STREAM NO.		2 (SORBER EXIT HEADER)		2-A (FLUE GAS EXIT FROM SORBER D-1)		2-B (FLUE GAS EXIT FROM SORBER D-1)	
COMPOSITION	M.W.	LB/HR	MPH	LB/HR	MPH	LB/HR	MPH
CO	28.011						
CO ₂	44.010	1,923,638	43,709.11	877,512	19,938.92	877,512	19,938.92
COS	60.075						
H ₂	2.016						
H ₂ O	18.015	483,814	26,856.18	211,896	11,762.21	211,896	11,762.21
H ₂ S	34.080						
N ₂	28.013	6,651,188	237,428.79	3,012,117	107,524.15	3,012,117	107,524.15
O ₂	31.999	322,185	10,068.60	147,251	4,601.75	147,251	4,601.75
S ₂	64.128						
SO ₂	64.063						
TOTAL		9,380,825	318,062.68	4,248,776	143,827.03	4,248,776	143,827.03

A

TABLE 39

HEATING CYCLE MATERIAL BALANCE

1-A (FLUE GAS INLET TO SORBER D-1)		1-B (FLUE GAS INLET TO SORBER D-2)		1-C (REGEN. GAS INLET TO SORBER D-3)		1-D (HEATING GAS INLET TO SORBER D-4)	
LB/HR	MPH	LB/HR	MPH	LB/HR	MPH	LB/HR	MPH
877,512	19,938.92	877,512	19,938.92	9628.50 17788.40	343.74 404.19	168,614	3831.27
211,896	11,762.21	211,896	11,762.21	5338.07 1414.00	2647.85 78.49	60,022	3331.76
3,012,117 152,206	107,524.15 4,756.57	3,012,117 152,206	107,524.15 4,756.57			626,953 27,682	22380.49 865.11
19,837	309.65	19,837	309.65	7.06	0.44		
4,273,568	144,291.50	4,273,568	144,291.50	34176.03	3474.71	883,271	30408.63
2-A (FLUE GAS EXIT FROM SORBER D-1)		2-B (FLUE GAS EXIT FROM SORBER D-2)		2-C (REGEN. GAS EXIT FROM SORBER D-3)		2-D (HEATING GAS EXIT FROM SORBER D-4)	
LB/HR	MPH	LB/HR	MPH	LB/HR	MPH	LB/HR	MPH
877,512	19,938.92	877,512	19,938.92	2492.42 28527.28 645.81	88.98 648.20 10.75	168,614	3831.27
211,896	11,762.21	211,896	11,762.21	1128.07 29056.75 18875.55	559.56 1612.92 553.86	60,022	3331.76
3,012,117 147,251	107,524.15 4,601.75	3,012,117 147,251	107,524.15 4,601.75	479.68 2545.22	7.48 39.73	626,953 27,682	22,380.49 865.11
4,248,776	143,827.03	4,248,776	143,827.03	83757.84	3521.92	883,271	30,408.63

B

TABLE 39 (CON'T)

STREAM NO.		3 (CLEAN FLUE GAS TO STACK)		4 (RECYCLE FLUE GAS)		5 (AIR TO RECYCLE FLUE GAS HEATER)	
COMPOSITION	M.W.	LB/HR	MPH	LB/HR	MPH	LB/HR	MPH
CH ₄	16.043						
C ₂ H ₆	30.070						
C ₃ H ₈	44.097						
C ₄ H ₁₀	58.124						
C ₅ H ₁₂	72.151						
C ₆ H ₁₄	86.178						
CO	28.011						
CO ₂	44.010	1,779,734	40,439.31	143,904	3269.80		
COS	60.075						
H ₂	2.016						
H ₂ O	18.015	447,631	24,847.66	36,183	2008.52	3,734	207.27
H ₂ S	34.080						
N ₂	28.013	6,153,531	219,663.85	497,656	17764.94	116,286	4151.09
O ₂	31.999	298,045	9,314.21	24,140	754.39	35,096	1096.78
S ₂	64.128						
SO ₂	64.063						
TOTAL		8,678,941	294,265.03	701,883	23797.65	155,116	5455.14

STREAM NO.		7 (RECYCLE FLUE GAS HEATER EFFLUENT)		8 (REGEN. GAS FEED TO SORBER)		9 (REGEN. GAS EFFLUENT FROM SORBER)	
COMPOSITION	M.W.	LB/HR	MPH	LB/HR	MPH	LB/HR	MPH
CO	28.011			9628.50	343.74	2492.42	88.98
CO ₂	44.010	168,614	3831.27	17788.40	404.19	28527.28	648.20
COS	60.075					645.81	10.75
H ₂	2.016			5338.07	2647.85	1128.07	559.56
H ₂ O	18.015	60,022	3331.76	1414.00	78.49	29056.75	1612.92
H ₂ S	34.080					18875.55	553.86
N ₂	28.013	626,953	22380.49				
C ₂	31.999	27,682	865.11				
S ₂	64.128					479.68	7.48
SO ₂	64.063					2545.22	39.73
CH ₄	16.043			7.06	0.44		
TOTAL		883,271	30408.63	34176.03	3478.71	83757.84	3321.92

A

TABLE 39 (CON'T)

(RECYCLE FLUE GAS)		5 (AIR TO RECYCLE FLUE GAS HEATER)		5-A (PILOT AIR TO RECYCLE FLUE GAS HEATER)		6 (NATURAL GAS TO RECYCLE FLUE GAS HEATER)	
LB/HR	MPH	LB/HR	MPH	LB/HR	MPH	LB/HR	MPH
						8221.39 402.04 101.42 99.39 77.20 45.67	512.46 13.37 2.30 1.71 1.07 0.53
13,904	3269.80						
86,183	2008.52	3,734	207.27	415	23.04		
97,656 24,140	17764.94 754.39	116,286 35,096	4151.09 1096.78	12,921 3,899	461.24 121.85	89.92	3.21
01,883	23797.65	155,116	5455.14	17,235	606.13	9037.03	534.65
8 (REGEN. GAS FEED TO SORBER)		9 (REGEN. GAS EFFLUENT FROM SORBER)					
LB/HR	MPH	LB/HR	MPH				
9628.50 17788.40	343.74 404.19	2492.42 28527.28 645.81 112.07 29056.75 18875.55	88.98 648.20 10.75 559.56 1612.92 553.86				
5338.07 1414.00	2647.85 78.49	479.68 2545.22	7.48 39.73				
7.06	0.44						
34176.03	3474.71	83757.84	3321.92				

TABLE 40

COOLING CYCLE MATERIAL BALANCE

STREAM NO.		2 (SORBER EXIT HEADER)		3 (CLEAN FLUE GAS TO STACK)	
COMPOSITION	M.W.	LB/HR	MPH	LB/HR	MPH
CO ₂	44.010	1,948,485	44,273.68	1,757,495	39933.99
H ₂ O	18.015	470,541	26,119.43	426,176	23656.74
N ₂	28.013	6,688,372	238,756.17	6,037,164	215509.86
O ₂	31.999	327,011	10,219.43	294,857	9214.56
TOTAL		9,434,409	319,368.71	8,515,692	288,315.15

STREAM NO.		4 (RECYCLE FLUE GAS) ¹		6 (NATURAL GAS TO PILOT BURNER OF B-1)	
COMPOSITION	M.W.	LB/HR	MPH	LB/HR	MPH
CH ₄	16.043			822.14	51.25
C ₂ H ₆	30.070			40.20	1.34
C ₃ H ₈	44.097			10.14	0.23
C ₄ H ₁₀	58.124			9.94	0.17
C ₅ H ₁₂	72.151			7.72	0.11
C ₆ H ₁₄	86.178			4.57	0.05
CO ₂	44.010	193,461	4395.84		
H ₂ O	18.015	46,749	2595.01		
N ₂	28.013	664,138	23,707.87	8.99	0.32
O ₂	31.999	32,509	1,015.94		
TOTAL		936,857	31,714.66	903.70	53.47

- NOTES: 1. The flow and composition given for Stream 4 are the same as that for Streams 1-D, 2-D and 7, which are to be changed from the values given in Table 39.
2. There is no Stream 5 flowing during the cooling cycle.

(2) Design Notes - Fixed Bed

(a) Process

1 - Selection of Base Case Design for Estimate

Although the actual sorption reaction has not been completely defined, kinetic data were presented by the USBM-Albany. These data coupled with the Amundsen rate equation provided a reaction rate constant which was used in the USBM-Bruceton sorption model to calculate sorber size and operating parameters. At the time it was felt that this procedure would provide a basis for a fixed bed design comparable to the fluid and dispersed phase cases. However, additional data for a fixed bed sorption would be required to confirm the present design before an actual plant was built.

A computer program (discussed previously in the Sorption Section) using the above model has been developed so that the effect of system variables upon design can be ascertained. Under initial consideration was the use of multiple, low-height, fixed-beds, with a large number of beds contained in a single vessel. Parallel trains of multiple vessels would be required since a cyclic method of operation is necessary, i.e., one train is regenerated while the other train is being loaded. Two main advantages derived from this type of operation are:

1. the reactor and regenerator are contained in the same vessel, and
2. attrition losses are minimized.

The problem areas in a system of this type are pressure drop, gas distribution, piping design, and catalyst life. It would also be necessary to remove the fly ash from the flue gas upstream of the absorber to prevent plugging of the sorbent beds.

Pressure drop considerations keep the bed heights low (1-5 feet) and since a large amount of gas must be processed, either the number of beds or the bed diameters become large. At low pressure drop and large diameters gas distribution becomes increasingly more difficult. On the other hand, should the number of beds be increased, to avoid distribution problems the piping arrangement would become more complex and pressure drop would be increased.

Sorbent life in fixed bed systems is an area in which little information has been reported. In order to make the fixed bed system economically feasible the sorbent should have no marked loss in activity or physical degradation over several hundred in-place regenerations.

As a first step, cylindrical vessels were assumed and the number of sorption stages calculated for various process conditions as summarized in Table 41. The information presented in Table 41 was obtained for each of two stream times and bed pressure drops, respectively 12 and 24 hours and 2 and 30 inches of water. The higher bed pressure drop was set by allowing this pressure drop to equal the normal ΔP of 2 inches of H_2O plus a one psi (~ 28 in. H_2O) increase, which is about the upper limit on pressure that can be obtained from a booster fan. Due to the problems of gas distribution and extremely low L/D ratios (pancake type vessels) it was decided to evaluate "panel type" arrangements for the sorber configuration rather than cylindrical shapes. Consequently, a thin rectangular shaped panel design was developed as the first basic design in the fixed bed evaluation.

Two different methods of contacting gases and solids which may have merit in the alkalized alumina process are offered by the Dorfan and Squires contactors. However, both the Dorfan and Squires contactors¹ differ somewhat from our

¹ AVCO Phase III Reports, Nos. 1-5

TABLE 41
NUMBER OF PARALLEL FIXED-BEDS REQUIRED
FOR
90% SORPTION OF SO₂

TIME (hrs)	24	24	12	12
ΔP (IN. H ₂ O)	2	30	2	30
BED HEIGHT (ft)	0.42	1.53	0.30	1.07
SORBENT VOLUME (ft ³)	76,710	76,710	39,075	39,075
# STAGES*	145	40	103	29

* Number of parallel fixed-beds required at a bed diameter of 40 feet.

sorption panel design in that they use a moving bed design, requiring a mechanical and/or pneumatic sorbent collection, feeding and transporting system as well as a separate regenerator. A brief description of the two systems is given below.

The Squires' sorber contains louvered panels to (1) direct gas flow through the sorbent, and (2) keep the sorbent from spilling out of the sorber (Figure J-103). Since these louvers are inclined to the horizontal the length of the path of the gas through the sorbent is relatively long. Thus in order to operate with a low pressure drop, a low gas velocity through the sorber is required; therefore to process the large volume of flue gas from a 1000 MW power plant, which is the basis for the present design, the contactor cross-sectional area must be large.

The Dorfan design (Figure J-104) uses louvers to direct the sorbent flow downward and yet provide a nearly true cross-flow design. The use of the louvers decreases the available cross-section for gas flow, however, necessitating larger or more numerous units than a true cross-flow sorber using a static bed.

Due to the attrition characteristics of the present sorbent, the concept of a static bed rather than a moving bed was the alternate chosen for study along with the fluid or dispersed phase systems. Since the design calculations for a fixed or static bed and a moving bed in plug flow are quite similar, it is felt that the fixed bed design will establish a sound reference point from which the Squires and Dorfan designs can then be evaluated if desired. In addition, it would appear that the present work on the fixed bed design should achieve the benefits of inexpensive containment of the sorbent in the optimum configuration that seen to be the objective of the Squires and Dorfan

designs. Accordingly, a detailed evaluation of the Squires and/or Dorfan systems was not made.

The basic static bed design uses a thin bed of sorbent to minimize bed pressure drop, but a higher pressure drop alternative, requiring a flue gas booster fan, was also evaluated. The first sorber design comprises a number of sorbent filled, rectangular shaped panels in parallel through which SO_2 -rich flue gas flows (Figure J-105). Each panel consists of a center core of sorbent held in place by the vertical walls of the panel which consist of a 100 mesh screen backed by a 2 mesh screen and a "subway" grate; in short, a sandwich arrangement in which the screening and grate form the sandwich wall. The top of each panel is blinded to act as a seal thus minimizing channeling of the gas should settling of the sorbent solids occur (Figure J-106). The panels are 40 feet in length with an active bed height of 20 feet plus an additional 2 feet for the seal, giving an overall height of 22 feet. The panels are inclined 23° from the horizontal to allow for gravity filling and draining of the sorbent (Figure J-107). A cylindrical design was later adopted as the basic unit because of mechanical requirements (see section (b)-1 below). This discussion on rectangular beds is included, however, since it applies equally well to the cylindrical design.

In order to prevent frequent start-up and shutdown of the regeneration and air compressors, a continuous operation schedule, for one complete sorption and regeneration cycle, utilizing four parallel trains of equipment was derived (Table 38). This operations schedule is arranged such that at any given time, two trains are in the sorption stage, one train is being regenerated, and one train is being heated or cooled. The operation schedule in Table 38 is broken down into eight steps of equal time increments, the increments

being a function of the onstream time required for sorption (e.g., if the elapsed time required to load the sorbent in the fixed bed units is 24 hours, the time increments are 6 hours each; similarly for a 12 hour sorption time the time increments are 3 hours each).

Two additional design cases (i.e., 6 and 4 hour sorption times) were added to those previously reported in Table 41. A summary of the design for each of these four cases is shown in Table 42. The number of on-stream sorption stages for each case shown in Table 42 was determined by obtaining the total cross-sectional area required for flow and dividing this area by the area per panel (40' x 20'). Under these conditions the number of cycles per year, number of panels per train, width per panel, length per train and plot area required were calculated and the results shown in Table 43. From the results shown in Table 43 it is seen that increasing the pressure drop by about 1 psi (from 2 to 30 inches of water), decreases the number of panels required by a factor of about 3.5. Since the higher pressure drop cases require the use of a flue gas booster fan, however, the resulting increase in operating costs must be balanced against investment savings to determine if there are net savings to be realized by increasing the pressure drop.

It is also apparent from Table 43 that as the sorption time decreases, the number and size of the panels (hence the sorbent inventory) decrease, but the number of sorption regeneration cycles per year increases. Comparing the number of cycles per year for the various sorption times shows a linear relationship; i.e., halving the sorption time doubles the number of cycles per year. A similar comparison of sorbent inventory and sorption time shows that the relationship is not quite linear; e.g., reducing the sorption time by a factor of 6 only reduces the inventory by a factor of 5.5. Thus as the sorption time decreases the sorbent would require more frequent replacement,

TABLE 42.
EFFECTS OF SORPTION TIME AND PRESSURE DROP
ON FIXED BED PARAMETERS

<u>TIME</u> <u>(hrs.)</u>	<u>ΔP</u> <u>(In. H₂O)</u>	<u>BED THICKNESS</u> <u>(In.)</u>	<u>GAS VELOCITY</u> <u>(ft/sec)</u>	<u>*NUMBER OF</u> <u>ON-STREAM</u> <u>SORPTION PANELS</u>
24	30	18-1/2	1.23	64
24	2	5	0.339	230
12	30	13	1.71	46
12	2	3-1/2	0.476	164
6	30	9	2.27	36
6	2	2-1/2	0.64	122
4	30	7	2.70	30
4	2	2	0.75	104

*Total number of panels is twice the number of on-stream sorption panels.

TABLE 43

EFFECT OF SORPTION TIME AND PRESSURE DROP ON SORBER DIMENSIONS

SORPTION ¹ TIME (hrs)	ΔP (In. H ₂ O)	SORBENT INVENTORY Thousand Pounds	CYCLES/ YEAR ² (-)	#PANELS/ TRAIN ³ (-)	THICKNESS/ PANEL (In.)	LENGTH/ TRAIN (ft-)	PLOT AREA ⁴ (ft ²)
24	30	6904	182.5	32	36½	97	20,370
24	2	6904	182.5	115	23	221	46,410
12	30	3517	365	23	31	60	12,600
12	2	3517	365	82	21½	147	30,870
6	30	1823	730	18	27	41	8,610
6	2	1823	730	61	20½	105	22,050
4	30	1259	1095	15	25	32	6,720
4	2	1259	1095	52	20	87	18,270

- ¹ Time required for one complete sorption-regeneration cycle is twice the sorption time
- ² Based on a 100% stream factor (365 days/year)
- ³ Four trains required
- ⁴ Width of plot is 210 feet in all cases

although the difference in sorbent life is small. For example if a 24 hour sorption time design had a one year sorbent life, use of a 4 hour sorption time would require a life of $12/5.5$ or 2.2 months to give the same sorbent costs. Since the labor and time required to drain and fill the sorber system would be appreciable, a sorbent life of only 200-300 cycles would probably require a long sorption time. Thus it is necessary to know the number of cycles the sorbent can withstand before complete economic evaluation of the fixed bed systems can be made. Since these data were not available, assumptions were required to complete the current design.

Calculations have shown the relationship between sorption time, bed pressure drop, bed thickness, and number of sorption panels required. Examination of these combinations shows that the lowest cycle time-high pressure drop case will produce the lowest investment in equipment and sorbent inventory. Although the lowest investment will not necessarily produce the lowest total annual costs, very brief, approximate estimates indicate that there probably is not a very large difference in operating costs (exclusive of capital charges) for the other high pressure drop cases. Brief approximate estimates also indicate that the high pressure drop cases will probably give lower total costs than the low pressure drop cases. Therefore, the high pressure drop case using a four hour sorption time has been selected for the base case design and estimate. It should be noted that the four hour case (eight hours for a complete sorption-regeneration cycle) is probably the minimum time that can be used since it provides only two hours for regeneration and one hour each for the heating and cooling operations, including the time required for switching gas flows.

Using the cylindrical design that was selected for the base case (see section (b)-1 below), bed thickness and number of beds were determined by use of the

sorption model proposed by the USBM-Bruceton. The bed surface area obtained from the model was increased by 20% due to blockage of the bed surface by the support steel, a 10% safety factor was then included to obtain the actual sorbing surface area, and the number of units were adjusted to allow for a symmetrical arrangement; as a result, the total surface area is about 50% greater than that calculated from the model. However, this allowance is not considered too large considering the lack of data for the fixed bed system.

2 - Safety Hazards

With regeneration and sorption occurring in the same vessel, a potential explosion hazard is created in that reducing gas, composed mostly of combustible compounds (H_2 and CO), will periodically come into contact with gases containing oxygen. That is, after the heating cycle ends, the ducts and sorption vessel will contain heating gas which has an oxygen content of about 3%. When the reducing cycle is started, therefore, combustible gases first entering the system will contact oxygen-containing gases at a temperature of about 1200°F, which could possibly result in an explosion or fire. Consequently, a study was undertaken to determine if the fixed bed system could be operated as presently conceived or would some modification be required, such as inert gas purging between cycles.

A literature search was conducted to determine if there is enough published information available to evaluate the present system without having experimental data. Essentially all of the references which were found that contained data on inflammability of gases referred to experimental work done by the Bureau of Mines and published in Bulletins 279 (first edition, 1928, revised and enlarged, 1930 and 1938), and Bulletin 503, dated 1952. The latter was

used for the evaluation of the fixed bed system.

Referring to Bulletin 503, Table 44, page 130 shows, for various gases or vapors, oxygen percentages below which no mixture is inflammable at "ordinary temperatures and pressures." For H_2 and CO, the combustible compounds in our reducing gas, these oxygen limits are 5.0% and 5.6% respectively, when the air is diluted with N_2 . The oxygen limits are increased to 5.9% when the air diluent is CO_2 . Thus, at ambient temperature our mixture would not be inflammable since the oxygen content is well below the minimum required for combustion, i.e., 3% actual vs 5% in O_2-N_2 mixtures. However, since our gases will be at 1200°F, the elevated temperature may cause the mixture to be hazardous and the problem becomes one of determining what effect temperature has on flammability limits.

As a first step, it was assumed that when the reducing gas is fed into the system and contacts the residual heating gas, combustion will occur until all the oxygen present is consumed. Knowing the volume of the equipment, the O_2 concentration, the temperature, and the pressure, the total heat liberated and the adiabatic temperature rise can be calculated. For the fixed-bed conditions considered, this temperature rise was found to be about 720°F, and the corresponding pressure increase would be 6.8 psi, assuming a pressure tight vessel. Since the vessels and ducts are not presently designed for pressure operation (maximum design pressure is 45 inches of water), a much more expensive design would result if the system had to withstand the above pressure increase. Therefore, it is important to the fixed bed evaluation to know if the reducing gas will burn when it enters the sorption vessels. It became necessary, therefore, to estimate the effect of temperature on flammability limits.

The effect of temperature on the H_2-N_2 flammability limits was determined as follows. Figure 6, page 19,

Bulletin 503 shows the influence of temperature on limits of flammability of H_2 in air for temperatures up to $400^\circ C$ ($752^\circ F$). The data in Figure 6 show a linear relationship between percent H_2 and temperature and it was assumed that these data could be extrapolated to $1200^\circ F$ ($550^\circ C$) for both the upper and lower limits of H_2 concentrations. Using the extrapolated limits for H_2 and air from Figure 6, the adiabatic temperature rise for these mixtures was then calculated and compared to the actual temperature rise. For the upper H_2 concentration limit the calculated temperature rise of the fixed bed process gases was essentially the same as that for the H_2 -air mixture from Figure 6, Bulletin 503. For the lower H_2 concentration limit the temperature rise of the process gases was somewhat higher than for the Figure 6 H_2 -air mixtures. In the latter case, however, the O_2 content of the H_2 -air mixtures was much greater than that of the actual process gases (20% vs 3%), and the effect of O_2 concentration on flammability limits is unknown. For the upper H_2 concentration case, the adiabatic temperature rise calculation indicates that a flammability problem may exist but no firm conclusion can be drawn at this time. That is, the present calculations are based on an assumed reducing gas composition and an extrapolation of data obtained from H_2 burning in air in small tubes (2.5 cm diameter and 150 cm long) for downward propagation of flame. Other data listed in Bulletin 503 (Table 1) indicate that the H_2 limits increase with increases in vessel size, and that direction of the flame propagation (i.e., upward, downward, horizontal) also influences flammability limits. Further, the strength of the ignition spark also has an effect on flammability limits.

As a result of the above discussed evaluation of the potential safety hazard arising from mixing combustible gases with O_2 -containing gas, the conclusion reached is that a hazard may exist but available literature data are insufficient to clearly define the flammability limits for the present fixed bed design. Therefore, the present preliminary fixed bed design will be made on the assumption that no hazard exists, but with

the reservation that if the fixed bed case is competitive with either of the other schemes (fluid bed or dispersed phase), additional detailed study of the flammability limits will be required. Further, with the proper reducing gas composition, as determined by regeneration studies, experimental data on the flammability limits of the actual process gases would be required before an actual plant could be designed and built.

3 - Heating and Cooling Gases

The heating gas flow was determined by calculating the heat required for a 600°F temperature increase in the sorbent and internal sorber structure, to which was added the slightly endothermic heat of reaction and the heat losses to the atmosphere from the sorber structure during maximum winter design conditions (25°F and 20 MPH wind velocity). Because the heat transfer in a fixed bed is very rapid, the solids and gas temperatures at any point are approximately equal, and therefore the inlet gas temperature was set as close as possible to 1200°F (regeneration temperature) since:

- (1) the allowable design stresses of the sorber structural steel decrease rapidly as the temperature increases above 1200°F; and
- (2) a lower temperature provides less risk of sintering the sorbent.

Because of these points the heating gas temperature was set at 1225°F. Since the system probably won't reach thermal equilibrium, due to the one hour cycle time, the average bed entrance temperature will be close to the desired 1200°F regeneration temperature.

The heating and cooling cycles require a source of 1200°F and 600°F gas respectively, and the oxygen content should be as low as practical to minimize the flammability hazard as discussed above. Note that 600°F gas is required for cooling since this is a fixed bed operation and the solids will be heated to the entering gas temperature. Since the sorber

effluent flue gas (i.e., the SO₂ free flue gas) is at 600°F, it was decided to use this gas for both the heating and cooling cycles. The cooling cycle uses the gas directly, but because the heating cycle requires gas at 1200°F, a recycle flue gas heater is provided wherein the necessary heat is supplied by burning natural gas (or sulfur-free fuel oil) and mixing the combustion gases directly with the recycle flue gas. It is assumed that the degree of thermal regeneration of the sorbent during the heating and cooling cycles will be small, so that the recycle gases can be returned directly to the main flue gas header without exceeding the maximum SO₂ limit of the stack gases.

The operating cycle of the fixed bed system is such that either heating or cooling gas is required at all times so that recycle flue gas blower operates continuously. The flue gas heater is required only one half the time, however, which means it has to be designed for frequent start-up and shutdown. Therefore, the furnace has been provided with two burners; a small pilot burner running continuously and a large burner operating intermittently, with each burner having its own air blower. The pilot burner is designed to supply enough heat to keep the combustion chamber refractory at its operating temperature when the preheater is not in use, i.e., during the cooling cycle. A vent line is provided to carry the pilot burner effluent gases from the flue gas heater to the main power plant flue gas header.

4 - Insulation

All ducts and equipment in contact with hot gases on one side and exposed to ambient conditions on the other will be insulated internally to minimize heat losses and to lower the design temperature of the materials of construction. To meet process requirements of good insulating properties and high abrasion resistance, a castable insulation (e.g., Grefco, HL-41) gunnited into place was selected. In selecting the

insulation thickness required, a before-taxes payout of about two-three years on incremental investment was used as the basis. That is the estimated incremental investment required for increasing insulation thickness must be paid for by increased fuel savings over a two-three year period. This criterion resulted in a six inch insulation thickness for all insulated metal surfaces. Since the life of the plant is greater than two-three years (4.5-6 years after taxes), using increased thickness of insulation probably would be economical but the savings would be too small to have an appreciable effect on overall costs.

The thickness of insulation required for the concrete sorber train itself was found to be greater than the six inches required for the metal surfaces. Brief, approximate estimates showed that concrete construction would be the most economical for the sorber vessel and since concrete must be kept below about 500°F, additional insulation was required. The concrete acts as an insulator itself so the temperature drop through the wall is much higher than for a metal wall. Calculations showed that multilayers of insulation would be the most economical means of reducing the inner wall temperature to about 400°F for the most severe process conditions that will be encountered. Consequently, two layers of low conductivity insulation (e.g., Superex M) four inches thick were used on the inside walls of the sorbers and one four inch layer of castable refractory (HL-41) was installed on top of the inner layers to produce a total thickness of twelve inches. The layer of castable was needed for abrasion resistance while the better insulating properties of the inner layers reduced the total thickness required.

(b) Mechanical

1 - Sorber Units

The initial proposed physical design of

the sorber is illustrated in Figures J-105 J-106 and J-107. Further study of that design indicated that expansion due to the thermal cycling, needed for sorption and regeneration, would pose severe design problems. Expansion along the 40 foot dimension of the sorber panel would be approximately 6 inches, when heated from ambient temperature up to the regeneration temperature of 1200°F, and approximately 3 inches of contraction and expansion would occur when cycling between the sorption and regeneration temperatures. Similar expansion problems, although not quite as severe, would also be occurring along the side walls of the sorber panels and in the inlet and outlet ducting. To alleviate these problems, modifications of the proposed sorber configuration were undertaken. It was decided that these modifications should follow the lines of furnace design where similar expansion problems are encountered.

In the revised coceptual design the sorber panels are supported by fixed structural members at the four corners of each sorber panel, J-108. Fixing the sorber panel at the corners keeps the structural shape of the sorber intact but forces the expansion inward. To allow for this expansion, slip joints are provided at the center of each of the four sides of the sorber panels. This arrangement allows the steel frame of the panel to move with respect to itself but produces very little movement between the frame and the sorbent, thus minimizing mechanical forces on the sorbent.

To provide space for further structural support to the lower sorber panel frame, the inlet and outlet ducts are placed on either side of the sorber panels rather than over and under the panels as in the previous design. The new design allows the lower sorber panel to rest on an insulating concrete base which provides both structural support and thermal insulation. The walls of the ducts are internally insulated so that thermal expansion of the steel ducts is negligible.

Another design modification is the elimination of the partitions which ran between the sorber panels (Figure J-105). In the new design (Figure J-109) SO₂ rich gas enters a duct common to two sorber panels; the gas flow then splits, going through each of the two panels for sorption. The clean gas then enters the ducts common to the adjoining panel where it flows into the clean gas header. The use of this design has a second beneficial effect in that in the old design the partition would have acted as a heat transfer surface during the heating and cooling cycles if left uninsulated, thereby decreasing the thermal efficiency of these cycles. Removal of this partition and its associated insulation should also result in a noticeable decrease in sorber cost as well as decrease the problems associated with the fabrication of the sorber sections. In the present design only the plates forming the gas seals at the ends of the panels act as heat transfer surfaces and need be insulated to increase the thermal efficiency of the heating and cooling cycles.

To form the duct common to two adjoining sorber panels a top, bottom, and side cover plate are required. Figure J-110 shows the proposed arrangement for these cover plates. The two channel or plate and angle sections, which form the sorber panel, overlap one another and are connected with slip joints at their side walls. The top plate of the upper channel has a cut-out to allow for expansion of the lower panel cover. The panel covers are anchored at the channel ends. At one channel end a fixed pin is used to force the thermal expansion vectors outward parallel to the cover's edges. At the corresponding panel end of the adjoining sorber panel, a slip pin is used to allow for expansion in the direction perpendicular to the length of the cover plate and to prevent rotational movement of the cover plate around the axis of the fixed pin. This causes the remaining expansion vector to be directed along the length of the panel cover. Since the panel covers rest on the

sorber panels and overlap each other at their free ends the duct is sealed, either admitting flow from the inlet header or to the outlet header. Figure J-111 shows a detailed view of the center junction of the sorber panel sides and the dimensions of the channels and cover plates required to seal the duct and allow for thermal expansion of the panels and covers.

Figure J-112 shows the sorber support detail. Since the sorber is symmetrical, the detail shown is typical of all four corner supports. The side view shows the upper and side sorber panel frames and covers, abutting at the upper left corner of the sorber, and their connection to the support beam which joins the sorber panel to the outer steel frame. Views A-A and B-B show the panel cover connections to the support beam and sorber panel frames. The support beam is offset to allow for expansion of one of the panel covers while rigidly fixing the next panel cover and sorber panel. Detail C (Figure J-113) shows the proposed screening arrangement which will remain essentially the same as was discussed in section (2) (a) 1 above; i.e., a sandwich arrangement with the sorbent encased by the grate and screening walls.

Overall sorber panel dimensions, length, width and bed depth, remain the same as before (Figure J-106). The distance between sorber panels (A), the width of the sorber panel covers (B) and the width of a sorber panel (C) along with the sorbent bed thickness (D) are given as a function of sorption stream time and bed pressure drop in Table J-98. It should be noted that these dimensions do not consider mechanical requirements.

The conceptual design of a fixed bed sorber panel as described above was next evaluated for structural and fabrication feasibility. These panels were originally designed

from process considerations such as pressure drop, bed thickness, etc., with only conceptual designs of key mechanical items such as sliding joints for thermal expansion, and structural supports. Having selected a base case as discussed in the process section above, a mechanical design was undertaken in sufficient detail to insure fabrication feasibility and to provide a sound basis for the cost estimate. As a result of this mechanical design it was found that the flat type sorber panel previously required an excessive amount of structural steel and consequently produced a very expensive design. A sketch of the cross-section of the sorber train using flat panels is shown in Figure J-114. This sketch which is drawn to a scale of 1/8" equals one foot, graphically illustrates the quantity of structural support required in that the overall dimensions are 72 feet wide by 59 feet, whereas the sorber panel is 40 feet by 20 feet. Further, the panels themselves require trusses between pairs, with tie rods holding the sides of each panel together, and additional miscellaneous framing is required. Because of the complicated and rather massive sorbent-containing vessels and supporting structure needed, it was decided to seek an alternate design which would offer a simpler and cheaper unit.

A cylindrical configuration for the sorber units was designed which gives substantial savings in fabrication costs. Since the major factor influencing the panel structural requirements is pressure drop through the panel (i.e., 30 inches of water is equivalent to about 150 pounds per square foot), a cylindrical shape gives a much lower cost because of its much higher inherent strength compared to a flat panel. This increased strength is of particular importance for the present case because the 1200°F design temperature reduces the allowable metal stresses to only about 4000 psi for the type 321 stainless steel used. As in the flat panel design, thermal expansion will be handled by providing sliding joints, which will be stellite and ground smooth.

A sketch of the cylindrical sorber design is shown in Figure J-115. As indicated by the sketch, this new design essentially comprises rolling the original flat panel into a cylinder, thereby greatly reducing structural requirements. Each of the cylinders has a mean diameter of 3 feet, a bed thickness of 7 inches, and a length of 22 feet. The length of the sorber units through which the flue gas flows is 20 feet; the extra two feet are provided to allow for sorbent settling. Gas flow is from the outside to the inside of the units.

Loading of the sorber units will be done by pneumatically conveying the sorbent to the top of the cylinders and gravity filling. A hopper truck equipped with a blower could be used for loading the units. When it is necessary to unload the units, the sorbent can be gravity dumped and removed by a front-end loader. Space under the sorber buildings is required for heat transfer purposes, i.e., to provide for adequate air circulation to avoid heat build-up in the vessel floor, and this space has been made large enough to permit passage of a front-end loader.

2 - Sorber Trains

The sorber building (or train) itself has concrete bottom and sides with a steel roof. There are twelve inches of insulation over the concrete sections and six inches over the steel. A sketch of the cross section of a sorber building is shown in Figure J-116. There are four sorber trains required with 6 rows of 14 sorber units in each train to give a total of 336 which, as discussed in Section (a) -1 above, provides 50% more surface than calculated from the model. Thus the superficial gas velocity through the beds is reduced from the value of 2.7 feet per second shown in Table 42 to 1.8 ft/sec. A transition piece is used to connect the inlet

and outlet ducts with the sorber buildings, so that the entire cross-section of the sorber is used for gas flow. A plan of the layout of the sorber trains is shown in Figure 56.

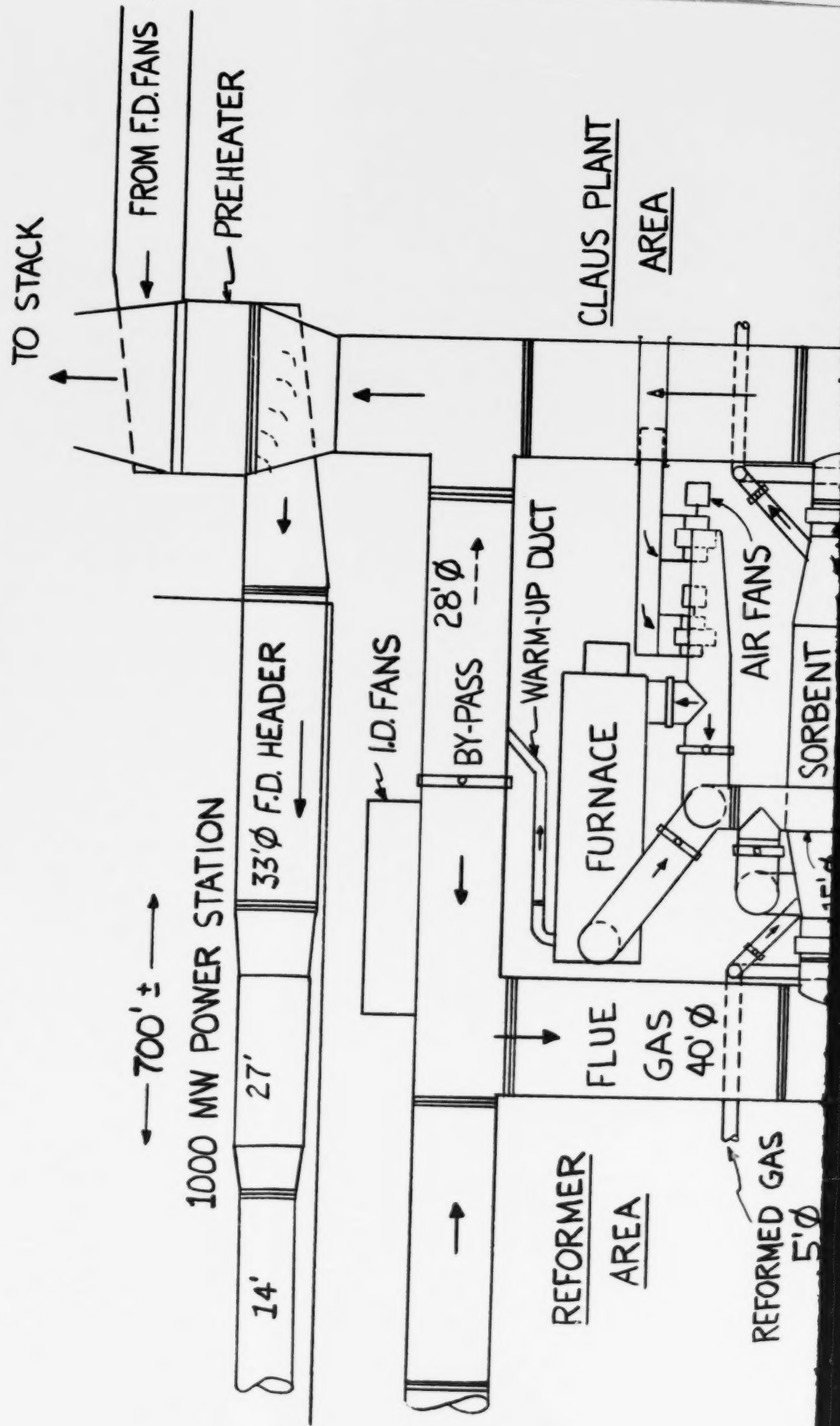
3 - Gas Ducts

The gas ducts are sized for 60 feet per second superficial gas velocity and a maximum pressure of 45 inches of water. Six inches of insulation on the inside are used to reduce the metal temperature to about ambient conditions and material of construction is carbon steel. The diameters of the various lines are: main flue gas ducts -- 40 feet; flue gas inlet and outlet branch ducts -- 28 feet; heating and cooling gas ducts -- 15 feet; and reducing gas ducts -- 5 feet. To minimize duct cost and maximize duct stiffness with minimum weight, cellular steel floor deck is used for the duct walls with curved ring trusses around the outside of the duct for support, stiffening, and tension stresses. The cellular floor deck is a readily available item and combines high rigidity with light weight, and also provides a smooth inner surface with maximum stiffness to support the insulation against duct vibration.

4 - Valves

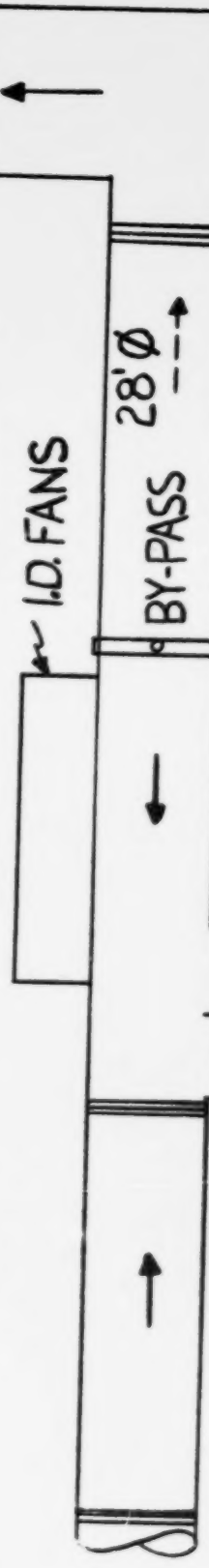
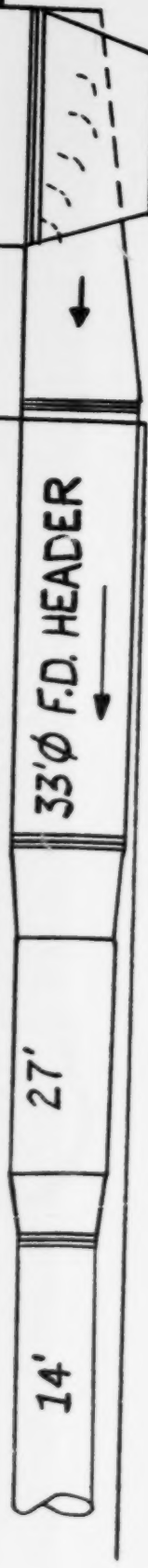
The large valves required for switching gas streams posed a problem in that valves of the size needed were not commercially available in a price range that could be tolerated. Consequently, various vendors were contacted to see if they could meet our process requirements with a suitable valve. The results of this search are included as Table J-99. Grove Valve and Regulator Company has tentatively designed and estimated, specifically for the fixed bed case, a retracted disc valve 20 feet in diameter, after conferring with MWK concerning process specifications. The gas ducts are 28 feet in diameter but a valve this size does not appear feasible so the 20 feet diameter valves are used. The higher gas velocity through these valves

FIGURE 56
FIXED BED SCHEME - CYLINDRICAL SORBER UNITS
GENERAL ARRANGEMENT

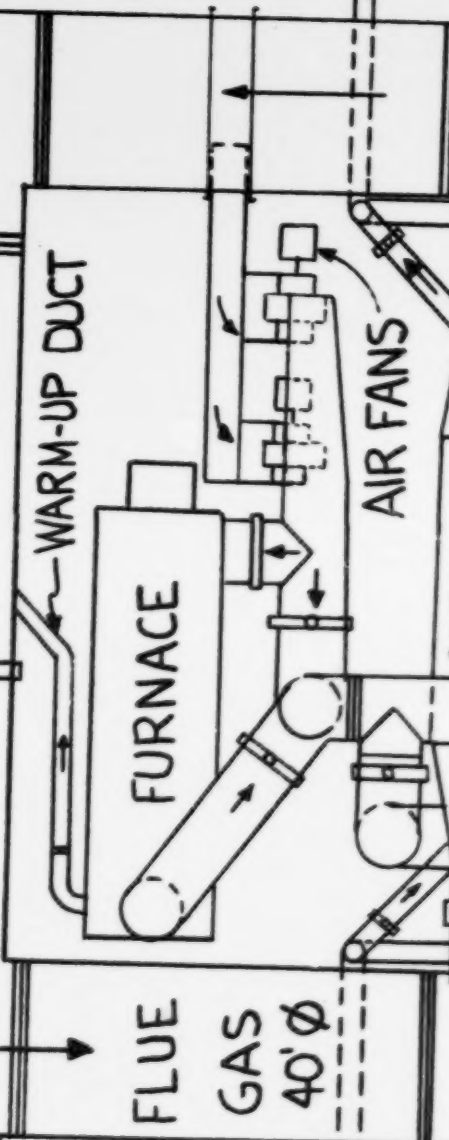


1000 MW POWER STATION

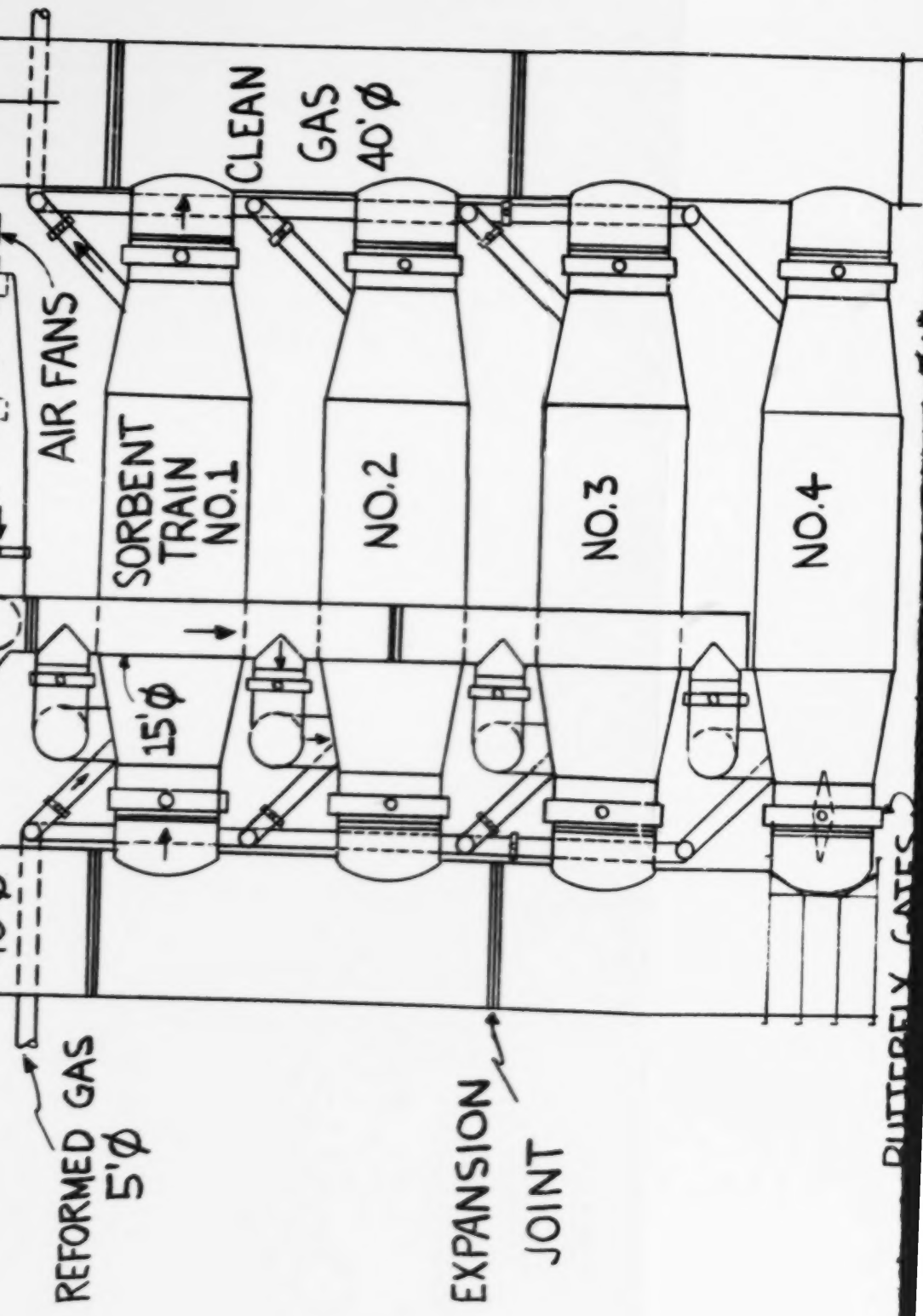
PREHEATER



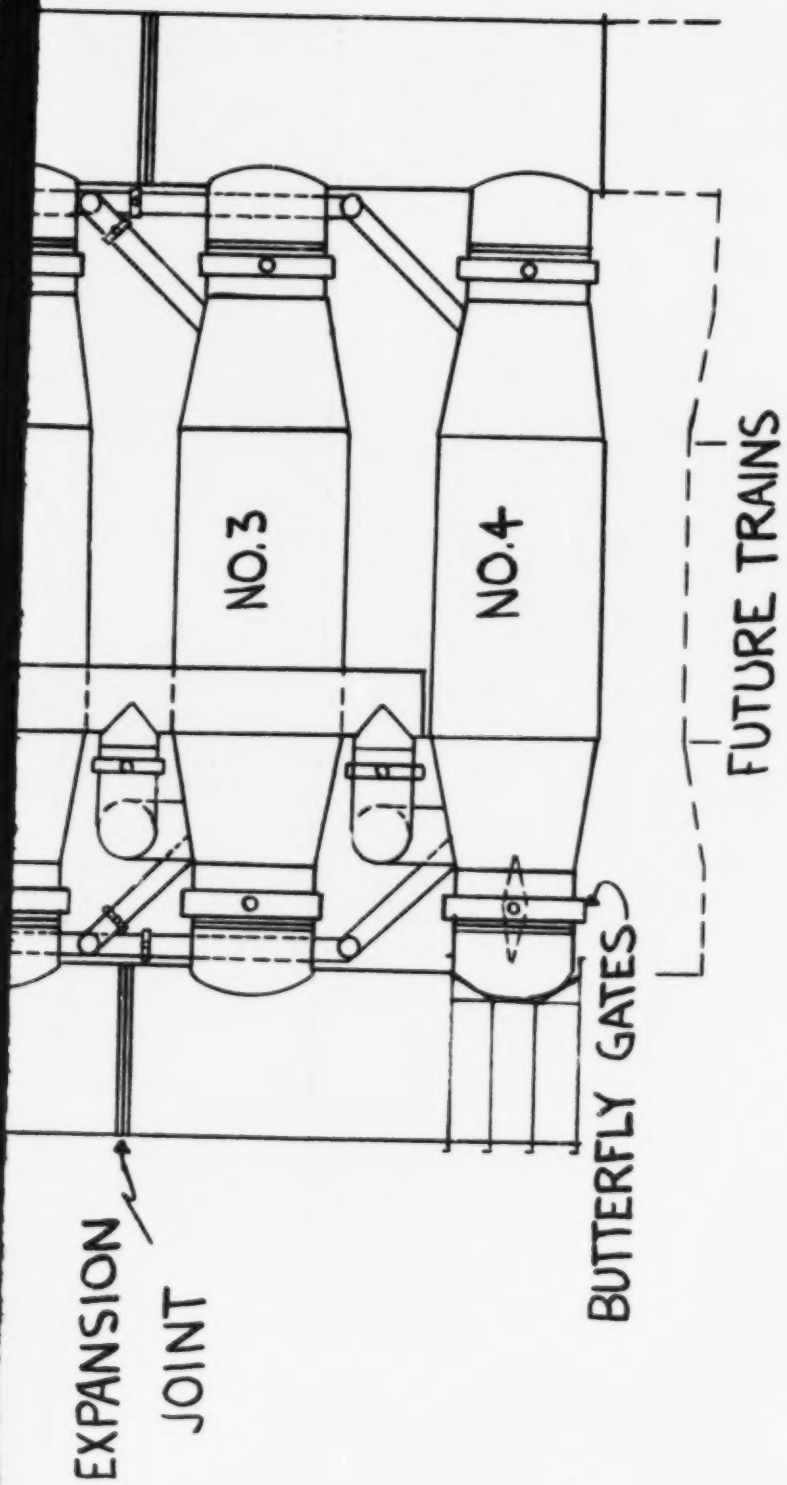
REFORMER AREA



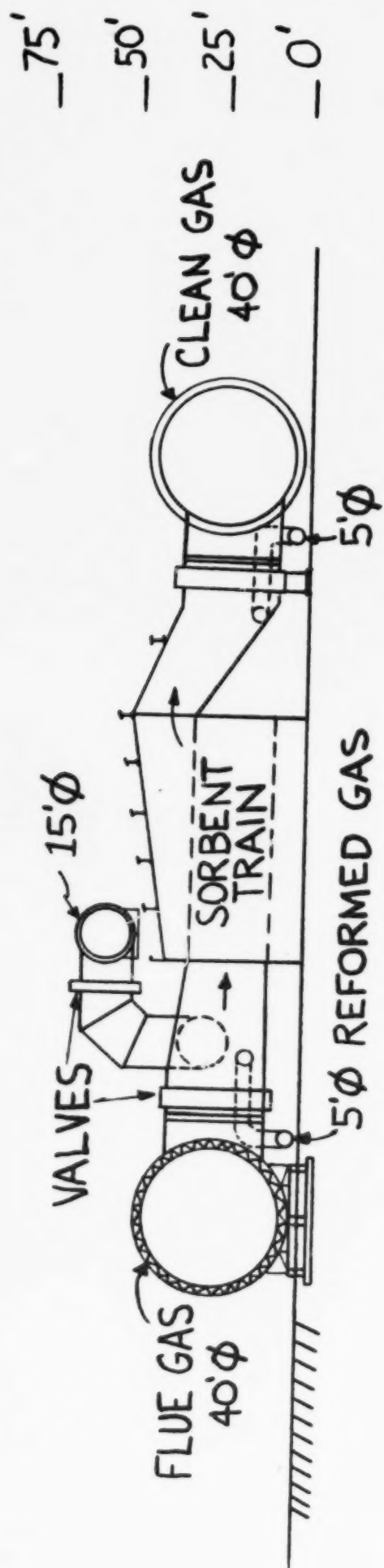
CLAUS PLANT AREA



DIFFERENTIAL GATES



PLAN



is not considered to be a problem. The initial preliminary valve design will probably have to be refined to include water cooling of the valve seats (to avoid the excessive thermal stresses in the cold duct walls that would result from connecting a hot and cold mass together), but this modification can easily be made. Fixed bed economics includes Grove's estimate for the large valves.

5 - Flue Gas Fans

The additional gas pressure drop caused by the fixed bed system requires the use of flue gas booster fans. Since the power plant itself already requires flue gas fans, use of these existing fans as the booster fans by increasing the discharge pressure was considered. The fixed-bed pressure drop is 30 inches of water and another 5 inches has been allowed for line losses, etc., so the total incremental pressure drop due to the fixed-bed system is 35 inches of water. Subsequently, it was found that increasing the discharge pressure of the existing fans would be impractical so an additional set of fans was included as part of the alkalized alumina process.

6 - Air Preheater Ductwork

The sorption reaction requires a temperature of about 600°F so the flue gas is withdrawn from the power plant circuit upstream of the power plant air preheater. The layout of the alkalized alumina plant is such that the power plant air preheater must be relocated, thus increasing the quantity of air ducts required. The cost of these additional ducts is included in the alkalized alumina plant investment.

d. Comparison of Processes

A brief comparison of the major design factors and key process features based on the final design of each process is given in Tables 44 and 45. It should be noted that although

TABLE 44
MAJOR PROCESS FACTORS - ALKALIZED ALUMINA

ITEM	FIXED BED	FLUID BED	DISPERSED PHASE
Sorption Temp., °F	600	634	658
Regeneration Temp., °F	1200	1400	1400
Solids Heating Method	Indirect	Direct	Direct
Regenerator Type	Fixed Bed	Fluid Bed	Moving Bed
Solids Transfer Method	None	Pneumatic	Pneumatic
Sorbent Density in Reactor, lb/CF	45	30	0.15
Reactor Gas Velocity, fps	1.8	5	25
Flue Gas Press. Drop, in H ₂ O	30	30	10
Sulfur Loading on Sorbent, %:			
In	4.0	2.6	0.5
Out	13.0	7.0	3.0
% Sulfur Removal from Flue Gas	100	90	90
Solids Circulation Rate, lb/hr	None	380,000	706,000
Number of Reactor Units	336	10	2
Approximate Size of Reactor Unit	3'φ x 22'	40' x 60'	40' x 185'
Approximate Plot Size	350' x 400'	250' x 400'	250' x 400'
Approximate Max. Elev. Above Grade	80'	135'	275'
Sorbent Inventory, lbs.	1,940,000	1,590,000	2,200,000

TABLE 45

RELATIVE COMPARISON OF FIXED, FLUID, AND DISPERSED PHASE SYSTEMS

	FIXED BED	FLUID BED	DISPERSED BED
1. Attrition Losses	Low	Medium	High
2. Integration into New Power Plant	Good	Good	Good
3. Integration into Existing Power Plant	Poor	Poor	Poor
4. Unusual Special Equipment Required	Large Valves	--	--
5. Compressor Required on Claus Feed Gas	Yes	No	No
6. Explosion Potential Exists	Yes	No	No
7. Fly Ash Accumulation on Sorbent	Probably High	Slight	Nil
8. Operation Gas Velocity Dependent	No	Yes	Yes
9. One Train Shut Down Required at Half Gas Flow	No	No	Possibly
10. On-Off Operation Required	Flue Gas Heater	None	One-Train
11. By-Pass Included	Yes	No	No
12. Space Required-Percent of Powerhouse	~70	~50	~50

some of the ratings listed in Table 45 are subjective in nature, it is believed that they accurately represent the relative merits of each process. The space needed for each process and shown as a percentage of that required by the powerhouse is calculated based on the approximate plot size and the area reported for TVA's Gallatin power plant. As such, the values reported are approximate in nature but do serve to point out that the space requirements of the alkalized alumina processes are large and particularly in areas of high cost real estate, could cause a substantial increase in capital investment.

All of the items listed in Table 45 have either been discussed in detail in other sections of this report and/or are self explanatory. There are two items which could have a major effect on the fixed bed design and probably should be specifically noted, viz., the explosion potential and fly ash accumulation on the sorbent.

When the regeneration cycle starts, reducing gas will come into contact with gases containing oxygen (i.e., the sorber unit contains the flue gas used for heating), thus creating a potential explosion hazard. Lack of experimental data for the specific system involved prevents a precise evaluation to be made at this time. If it became necessary to purge the sorber with an inert gas before and after each regeneration, the cost would be significantly increased. Experimental data in this area are essential before a fixed bed unit is built.

The second item noted above, i.e., fly ash accumulation on the sorbent, is due to the fact that the extent to which the fixed bed will act as a filter is presently unknown. It is possible that the sorbent could filter out fly ash such that the pressure drop through the bed becomes excessive and/or the sorbent becomes coated with fly ash and loses its SO_2 removal ability. Again, experimental data are required before a plant is built.

e. Reformer, Claus Plant, and Precipitator

The commercial scale designs MWK have developed are based on presently available experimental data from the several contractors (e.g., AVCO, USBM, W. R. Grace) working on the alkalized alumina process with various assumptions required where data are lacking. Three basic designs have been developed (i.e., fixed bed, fluid bed, and dispersed phase) with the objective of determining which of the three, based on both technical feasibility and process economics, would be the best process for further development. Since several sections of the processes are common to all three schemes, these sections were not included in the preliminary designs. Therefore, in order to obtain a complete picture of process economics, it was necessary to estimate these additional sections. The remaining sections which are common to all three designs are discussed below:

(1) Regeneration Gas Plant

For the base case designs it was decided to use a steam-reformed natural gas as the reducing gas needed to regenerate the loaded sorbent. A flow sheet P1374-B, of the reformer plant, is shown in Figure 57. Natural gas feed is desulfurized in the activated carbon guard drums before entering the reformed furnace since sulfur will poison the reformer catalyst and therefore must be removed from the feed gas upstream of the reformer. In the reformer furnace natural gas and steam flow through catalyst packed tubes and react to form H_2 , CO, and CO_2 . The heat of reaction is supplied by burning additional natural gas with air outside the tubes. Reaction conditions to produce the desired gas composition for the present design were determined to be 50 psia and 1600°F. The effluent flue gas from the furnace is at 490°F and this gas is added to the power plant flue gas stream downstream of the sorber, and thus passes through the air preheater before being vented to the atmosphere.

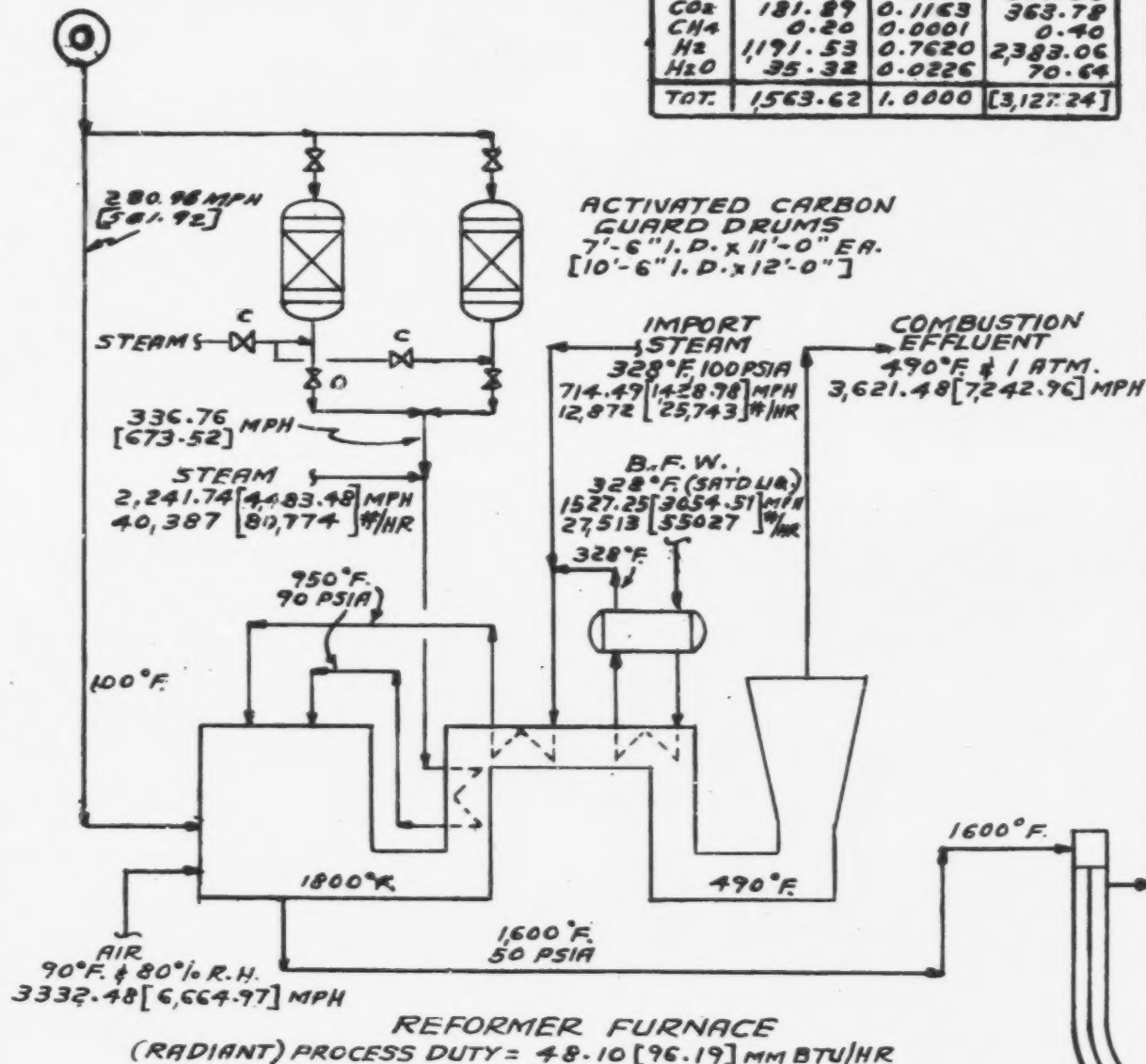
NATURAL GAS FEED
617.72 [235.44] MPH

TO SORBENT
REGENERATOR

	MPH	MF	[MPH]
CO	154.68	0.0990	307.36
CO ₂	181.89	0.1163	363.78
CH ₄	0.20	0.0001	0.40
H ₂	1191.53	0.7620	2383.06
H ₂ O	35.32	0.0226	70.64
TOT.	1563.62	1.0000	[3,127.24]

1400°F
37 PSIA

FOR FIX
TOTAL G
INCREA
[3,474.7
1200°



NOTES: 1. FLOWS CORRESPOND TO THOSE ON THE
FLUID BED SOPTION PROCESS FLOWSHEET
P3198-D.

2. THE NUMBERS SHOWN IN BRACKETS
INDICATE THE REQUIRED FLOWS, DUTIES
AND SIZES FOR A SINGLE REGEN. GAS
PLANT FEEDING TWO TRAINS OF EQUIPMENT
SHOWN ON FLOWSHEET P3198-D.

TO SORBENT
REGENERATOR

MPH	MF	[MPH]
154.68	0.0990	307.36
181.89	0.1163	363.78
0.20	0.0001	0.40
1191.53	0.7620	2383.06
35.32	0.0226	70.64
1563.62	1.0000	[3,127.24]

1400°F
37 PSIA

FOR FIXED BED CASE
TOTAL GAS FLOW IS
INCREASED TO
[3,474.71 MPH] @
1200°F.

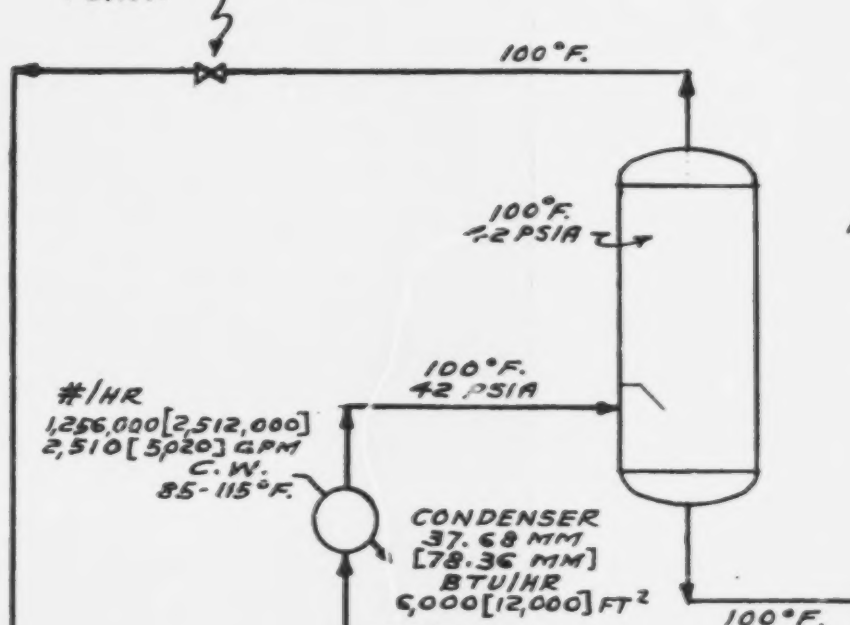
ED CARBON
DRUMS
x 11'-0" EA.
x 12'-0"

RT
AM
00 PSIA
78 MPH
43 #/HR
COMBUSTION
EFFLUENT
490°F & 1 ATM.
3,621.48 [7,242.76] MPH

(ATDUA)
1.51 MM/H
27 %

490°F
FACE
9] MM BTU/HR

FOR FIXED BED CASE
PRESSURE IS REDUCED
TO ~1-2 PSIG AT THIS
POINT.



#/HR
1,256,000 [2,512,000]
2,510 [5,020] GPM
C.W.
85-115°F

CONDENSER
37.68 MM
[78.36 MM]
BTU/HR
5,000 [12,000] FT²

350°F
44 PSIA

41 PSIA

W.H. BOILER
19.25 [38.50] MM
BTU/HR

18 F.W.
200°F
50 PSIG, 298°F
STEAM

1066°F
46 PSIA

1056.5 [2,113] MPH
19,039 [38,078] #/HR
1,450 [2,900] FT²

	MPH	MF
CO	154.68	0.0476
CO ₂	181.89	0.0559
CH ₄	0.20	0.0001
H ₂	1191.53	0.3664
H ₂ O	1723.33	0.5300
TOT.	3,251.63	1.0000

[6,503.26]

REGEN. GAS HEATER REGEN. GAS PREHEATER

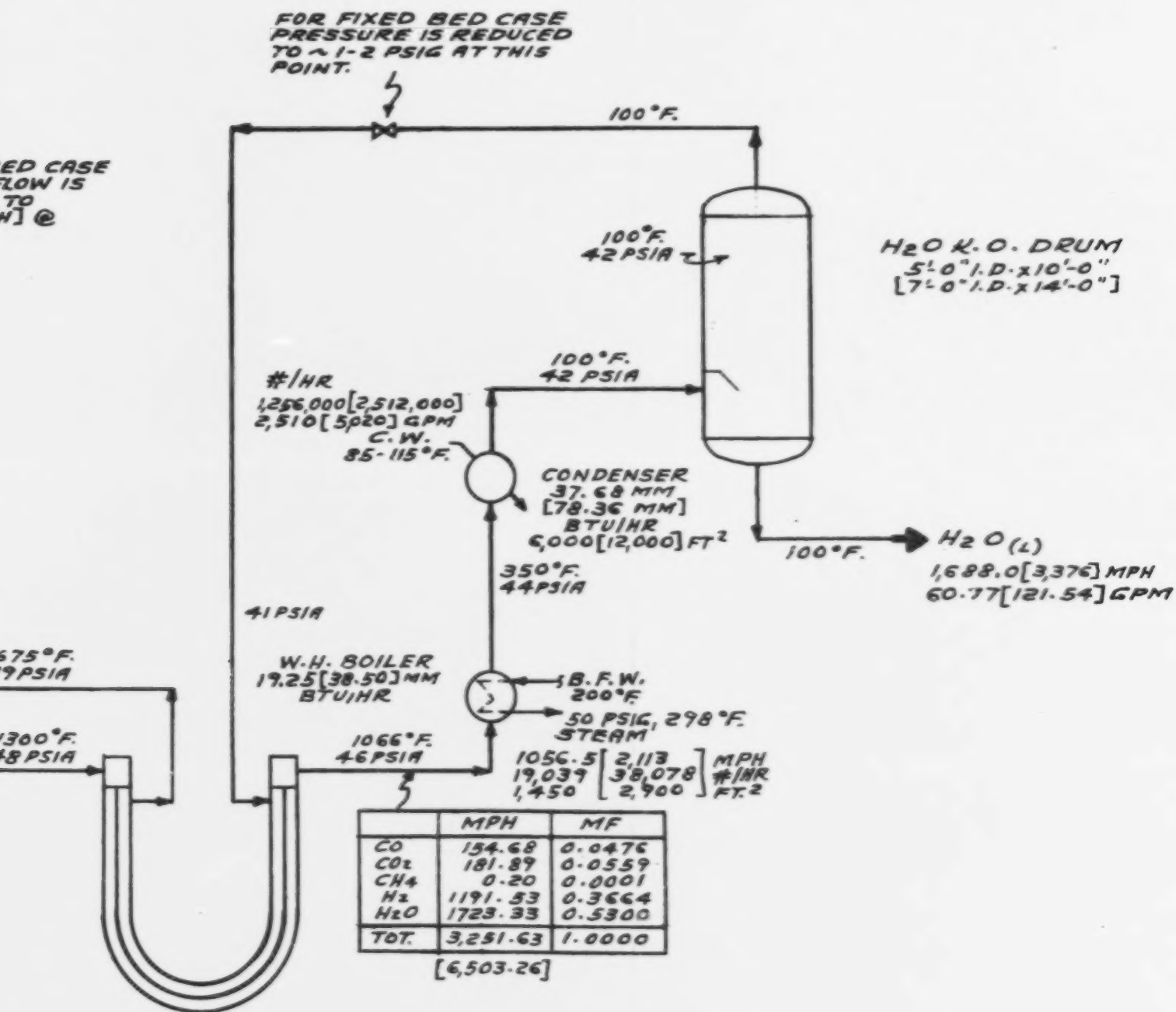
8.86 MM BTU/HR (900 FT²) 6.69 MM BTU/HR (375 FT²)
[17.72 MM BTU/HR 1800 FT²] [13.38 MM BTU/HR 750 FT²]

IN THE
SHEET

TS
DUTIES
GAS
EQUIPMENT

REGENERATION GAS P
FOR AA FLOWSHEET

1	GENERAL	2-27-70	GND	ENGR. G.M.D.	THE M.
				DRAWN: F.P.R.	
				CHECKED:	FI
NO.	REVISION DESCRIPTION	DATE	BY	CHK.	APPROVED:
	ISSUED FOR FABRICATION				DATED: 8-31-69
	ISSUED FOR CONSTRUCTION				CLASS



REGENERATION GAS PLANT
FOR AA FLOWSHEETS

1	GENERAL	2-27-70	END			ENR. G. M. D.		THE M. W. KELLOGG COMPANY			
						DRAWN: F. P. R.		a division of PULLMAN INCORPORATED			
						CHECKED:		FIGURE 57			
NO.	REVISION DESCRIPTION	DATE	BY	CHK.	APPROVED:			6045	P1374-B		
ISSUED FOR FABRICATION		ISSUED FOR CONSTRUCTION				DATED: 8-31-69	CLASS	AREA	JOB NO.	DRAWING NO.	

The product gases from the reformer contain over 50% water and since a "dry" gas is needed for regeneration, this water must be condensed. The regenerator temperature has been set at 1400°F which is also the desired temperature for the reducing gas feed. Thus the heat exchanger train has been arranged such that the cooled, dried reformed gas is preheated by exchange with the hot effluent from the reformer furnace. The preheating operation requires two stages of exchange in series: 1) a regeneration gas heater where the dry reformed gas is heated from 675° to 1400°F by cooling the reformer effluent from 1600° to 1300°F, 2) a regeneration gas preheater where the dry gas is heated from 100° to 675°F by further cooling the reformer outlet gas from 1300 to 1066°F. The temperature of the wet gas stream effluent from the regeneration gas preheater is reduced from 1066° to 350°F by generating 50 psig steam in the waste heat boiler. Finally, the water is condensed by exchange with cooling water and the resulting gas-liquid mixture separated in the water knock-out drum. The dry gas, containing some 2% water, is preheated as described above and sent to the regenerator. The dried, preheated reformed gas is at about 37 psia which provides an ample allowance for friction losses and control valves since the maximum pressure in the sorber is 30 psia.

The flow rates shown on Pl374-B are for the fluid bed and dispersed phase cases. The reducing gas quantity required for the fixed bed case is shown on the outlet stream only but if intermediate values are desired they can be prorated using the ratio of the two product streams shown.

To date, the maximum allowable water content in the reducing gas to the regenerator has not been determined and the present designs are based on "dry" gas (i.e., about 2% water). If later data show that higher water concentrations can be tolerated, then the reformer can be redesigned to produce the regenerator feed gas directly thus eliminating the cooling and reheating operations.

An evaluation of this alternative reformer design will be made in the phase 3 work. ..

(2) Claus Gas Pre-Treatment

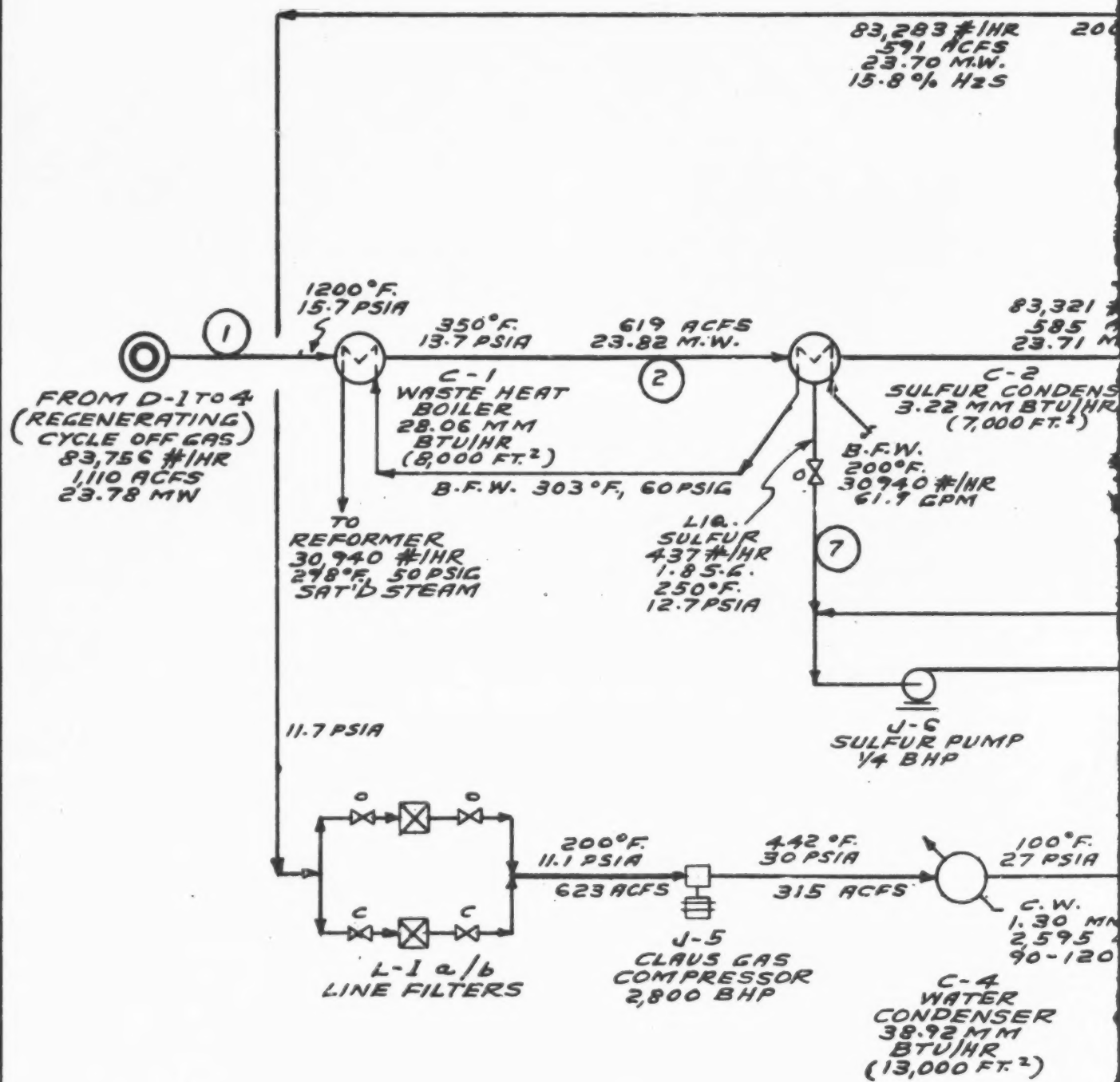
The regenerator gas effluent in all three of the present process designs contains about 18% H_2S , and greater than 40% H_2O . In addition, equilibrium calculations have shown that there will probably be some elemental sulfur present as vapor. It was originally planned to condense the water from the regenerator exit gas, thereby increasing the H_2S concentration to about 30% and thus reduce the size of the Claus plant. Further study showed, however, that because of the sulfur vapor present in the gas, cooling and condensing the water would also condense the sulfur. Further, because of the temperature range and sulfur concentrations involved, the equipment required became complicated and expensive; i.e., the sulfur temperature-viscosity relationship necessitated several steps involving quench towers, scraped surface exchangers (or equivalent type equipment), the cost of which would more than offset the incremental cost of the Claus plant due to a dilute H_2S feed. Therefore, for the fluid bed and dispersed phase cases, no pretreatment to the regenerator off gas is used other than a waste heat boiler for heat economy. The feed to the Claus reactor should be about 400°F and since the regenerator effluent is at 1400°F, the gas is cooled to the desired temperature by generating 50 psig steam. A credit will be taken for any steam in excess of that needed for the alkalized alumina plant.

The fixed bed case does require a pretreatment section, however, because the fixed bed regenerator is at atmospheric pressure and the off-gas must be compressed since the pressure drop through the Claus plant is about 10 psi. Limitations on the discharge temperatures of the compressor results in a maximum inlet

gas temperature of about 250°F for the pressure range involved, and cooling the gas to this temperature condenses the sulfur vapor present. A process flow scheme, P1375-B, for this fixed bed regenerator off gas treatment and compression is shown in Figure 58.

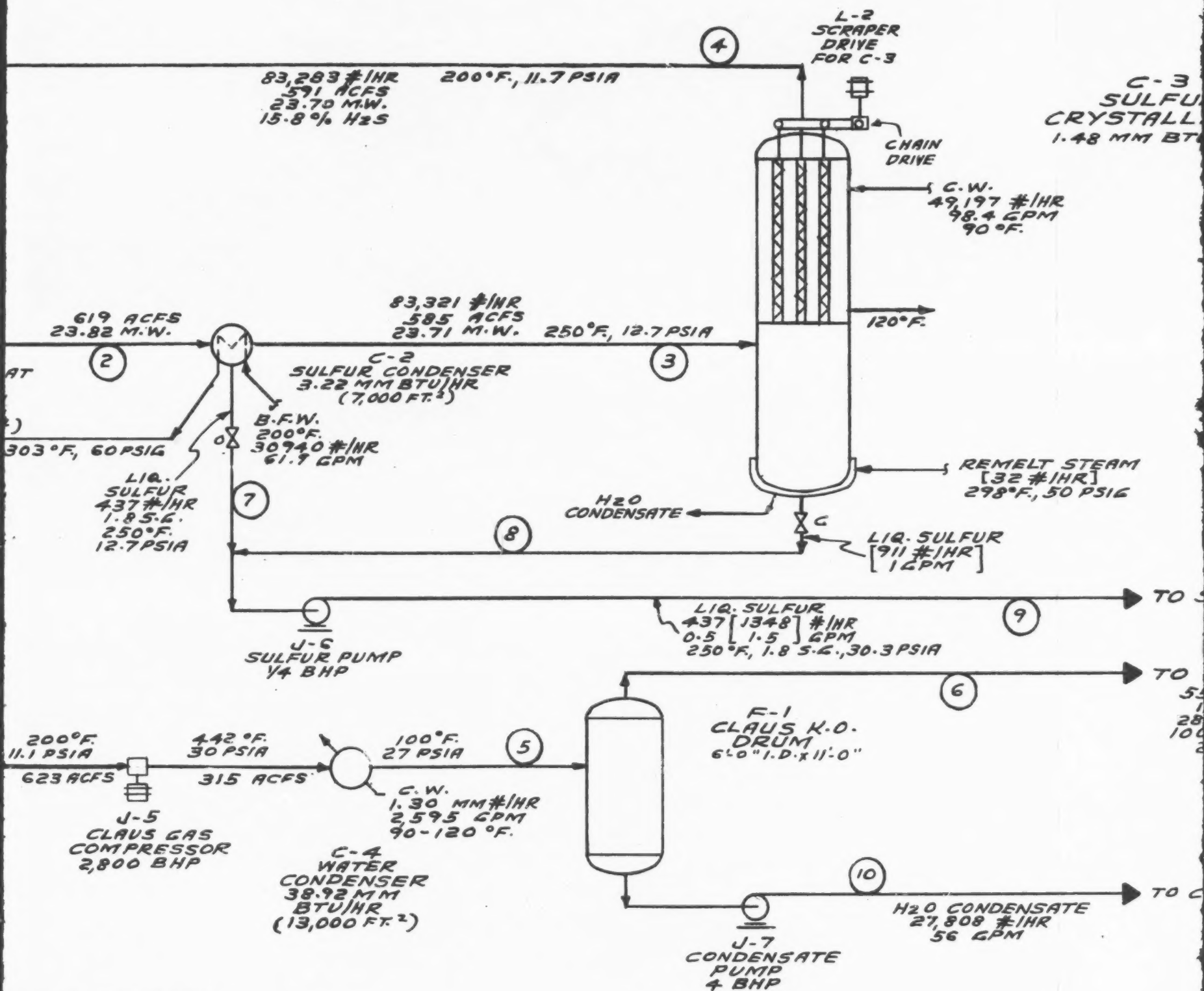
A brief process description for the fixed-bed Claus gas pretreatment section is as follows: referring to Figure 58, the hot gaseous effluent from the regenerator passes through a waste heat boiler, C-1, where it is cooled to 350°F by generating 65 psia steam. From C-1, the gas flows through a sulfur condenser, C-2, where most of the sulfur vapor is condensed to liquid sulfur at 250°F by exchange with the boiler feed water for C-1. At 250°F liquid sulfur will flow readily and is pumped to the main sulfur storage pit. The effluent gas from C-2 is sent to the water-cooled, scraped surface C-3 sulfur crystallizer (or desublimer) and cooled to 200°F thereby causing the remaining sulfur vapor to be deposited as sulfur crystals on the cold tubes. The sulfur crystals are continuously scraped from the tube walls and fall by gravity into the steam-heated bottom section of C-3 where they are melted and heated to 250°F and then pumped along with the condensed sulfur from C-2 to the sulfur storage pit.

The effluent gas from C-3 passes through a guard filter, L-1, which removes any entrained sulfur particles and is then compressed to 30 psia in the Claus gas compressor, J-5. The J-5 discharge stream is cooled to 100°F in the C-4 water condenser wherein most of the water is condensed, thereby increasing the H_2S concentration in the gas stream to about 27%. The liquid water and gas are separated in F-1 knockout drum and the dried compressed gas is sent to the Claus unit for conversion to elemental sulfur.



NOTES: 1. [DESIGN VALUE] WHERE DIFFERENT FROM NORMAL.
 2. REMELT STEAM TO C-3 IS ON INTERMITTENT FLOW.

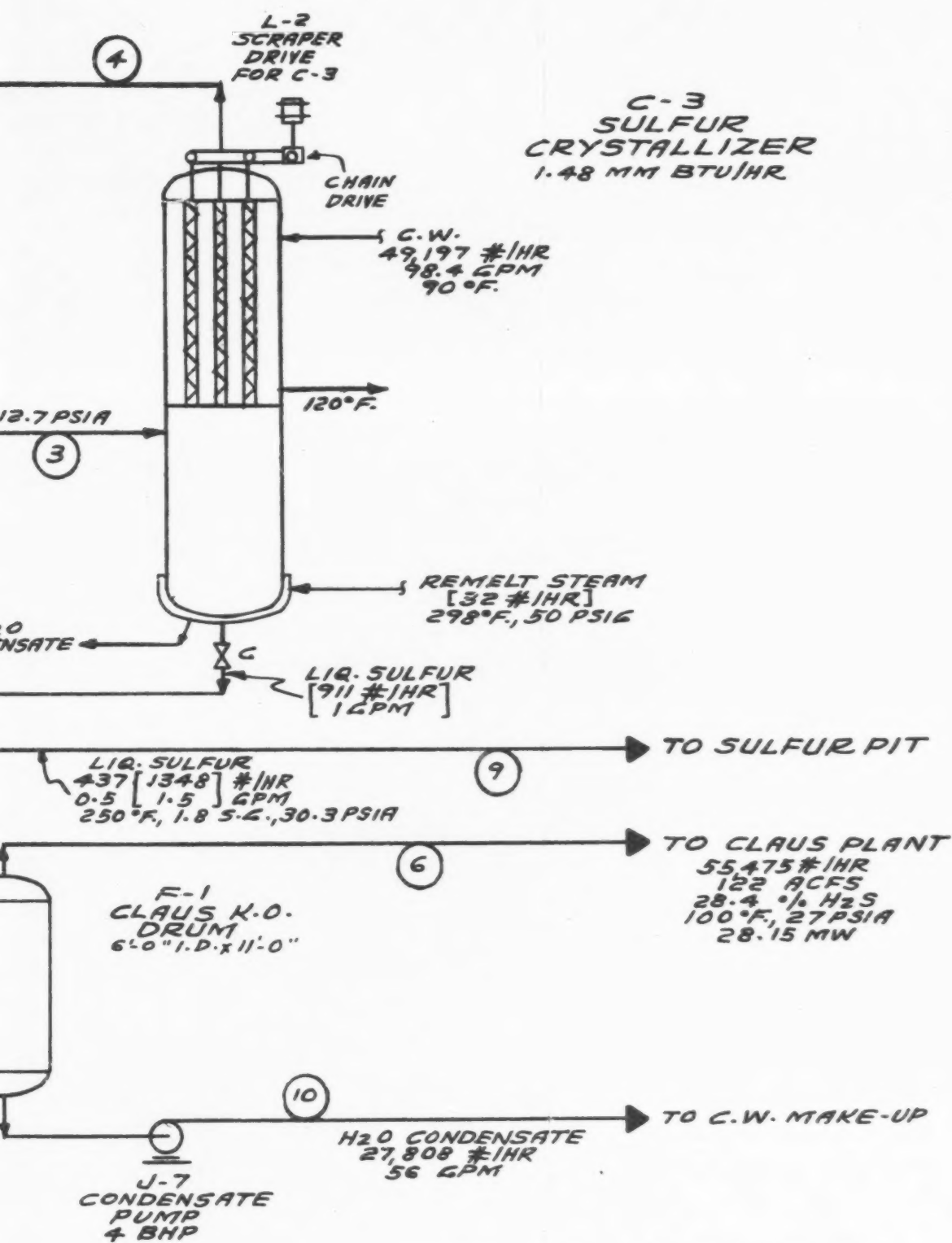
DEFIANCE



WHERE DIFFERENT
M TO C-3 IS ON
T FLOW.

FIXED BED FLOW
CLAUS GAS PRE-TRE

1	GENERAL	2-27-70	GMD	ENGR: G.M.D.
				DRAWN: F.P.R.
				CHECKED:
NO.	REVISION DESCRIPTION	DATE	BY	CHK.
	ISSUED FOR FABRICATION			ISSUED FOR CONSTRUCTION
				DATED: 8-31-67



FIXED BED FLOW SHEET
CLAUS GAS PRE-TREATMENT

1	GENERAL	2-27-70	GMD	ENER: G. M. D.	THE M. W. KELLOGG COMPANY a division of PULLMAN INCORPORATED			
				DRAWN: F. P. R.	FIGURE 58			
				CHECKED:			6045	P1375-B
NO.	REVISION DESCRIPTION	DATE	BY	CHK.	APPROVED:			
ISSUED FOR FABRICATION		ISSUED FOR CONSTRUCTION		DATED: 8-31-67	CLASS	AREA	JOB NO.	DRAWING NO.

C

It should be noted that since it is necessary to remove the sulfur, the water can be easily condensed thus upgrading the Claus feed gas. The fixed bed case, therefore, has a more concentrated feed gas for the Claus plant than the fluid bed or dilute phase processes.

(3) Claus Plant and Incinerator

As discussed above, the Claus plant is identical for the dispersed phase and fluid bed cases but is somewhat different for the fixed bed process. The cost of the gas pretreatment and compression is included as part of the Claus plant investment for the fixed bed scheme.

The Claus plant itself is a typical installation and comprises a burner, reactors, heat exchangers, and sulfur separators. One-third of the H_2S in the feed gas is converted to SO_2 by direct combustion in the burner, the effluent gases cooled to $400^\circ F$ by generating 50 psig steam, and the $400^\circ F$ gas stream then passes through the reactor where sulfur is formed:



Two stages of reactor are used to increase the efficiency of sulfur recovery. The exit gases are cooled to about $260^\circ F$ in the heat exchangers and then flow into the separator from which molten sulfur is pumped to storage.

About 90% of the sulfur in the feed gas is recovered as molten sulfur so the exit gases from the final separator contain about 10% of the entering sulfur as H_2S and SO_2 . If released directly to the atmosphere this gas would be a source of air pollution, and it may have to be recycled to the flue gas sorber after the H_2S has been converted to SO_2 in the Claus incinerator. The total volume of gas recycled is only 2-3% of the total flue gas feed so it has been assumed that no adjustments to the present reactor design are required because of the recycle gas. It has

been also assumed that the additional sulfur due to the recycle stream can be sorbed by letting the sorbent loading be increased by 10%, by increasing the sorbent circulating rate, or some combination of these two procedures. The additional sulfur pickup by the sorbent owing to the recycle stream would cause the reducing gas consumption in the regenerator to be increased by about 10%. Consequently the presently assumed reducing gas utilization of 80% would be increased to 88% for the same size reformer, or alternatively, a larger reformer would be needed. However, it has not been established that recycle is required, and comparisons would not be affected since all three processes would suffer essentially the same penalty, and therefore, because the effect of recycle on process design and economics is not significant in any case, it has been neglected in the present evaluation.

Since H_2S will probably not be sorbed by the alkalized alumina, it is necessary to convert the H_2S to SO_2 . This is done by heating the Claus effluent gas to about $1200^\circ F$ at which temperature the H_2S reacts with oxygen to form SO_2 . The gases are heated to $1200^\circ F$ in an incinerator by combustion of natural gas and air, and the excess combustion air supplies the oxygen needed to convert the H_2S to SO_2 .

(4) Electrostatic Precipitator

In all three of the present designs a larger electrostatic precipitator is required for the power plant, and the incremental cost of this precipitator is charged to the alkalized alumina process. In the fixed bed and the fluid bed cases, it has been assumed that the precipitator is needed upstream of the reactor to prevent excessive fly ash build-up since each of these systems will act as a filter. The extent of fly ash build-up is presently unknown but it seems highly probable that feeding the untreated flue gas directly into either system would cause blinding

of the sorbent, hence excessively high pressure drops, in the fixed bed case, and very high internal circulating loads of fly ash, causing high pressure drops and overloading of the reactor cyclones, in the fluid bed scheme. Thus, a relocation of the precipitator to a position upstream of the reactor and therefore upstream of the air preheater, results in an increased flue gas volume of about 40% because of its higher temperature, i.e., about 600°F instead of about 300°F. With a larger gas volume to be treated the precipitator size and cost are correspondingly increased. This increased cost is directly caused by and thus charged to the alkalized alumina process.

The fly ash does not affect the sorbent in the dispersed phase design, based on pilot plant results, and therefore, the electrostatic precipitator does not have to be relocated. Removal of the SO₂ from the flue gas upstream of the precipitator does lower the collection efficiency, however, and the precipitator size and cost are again increased. Values of precipitator efficiency as a function of the sulfur content in the fuel are reported in the literature¹ and an extrapolation of the data indicates a decrease of about 40% for the present process conditions. Thus the incremental cost of the electrostatic precipitator is about the same for all three designs and this cost is included in the total investment for each system.

(5) Power Plant Air Preheater

Standard power plant practice is to install an air preheater in the exit flue gas stream whereby the entering combustion air is heated by exchange with the effluent flue gas whose temperature is reduced from about 650°F to about 300°F.

¹ Reese, J. T., and Greco, J., "Experience with Electrostatic Fly-Ash Collection Equipment Serving Steam-Electric Generating Plants", J. AIR POLL. CONT. ASSOC., 18 (8), 524 (Aug. 1968).

As a result of installing an alkalized alumina plant both the volume and temperature of the effluent flue gas are increased. That is, the effluent gas from the solids heater and the solids transport air are added to the flue gas and in addition, the hot regenerated solids are cooled by the flue gas. Initially, no incremental cost was added to the air preheater because of the higher temperature and flow rates, based on phone conversations with a vendor who stated that this equipment is normally designed for increases up to 20%. However, subsequent written inquiries did in fact, result in cost increases to the air preheaters. This additional cost is a direct result of and therefore charged to the alkalized alumina plant.

f. Final Sorber Design

The original base case designs for both the fluid bed and dispersed phase schemes included a solids cooler to reduce the sorbent temperature from the regeneration temperature of about 1400°F to the sorption temperature of about 600°F. As an alternative design, it was decided to eliminate the solids cooler and return the regenerated sorbent directly back to the reactor without prior cooling. Subsequently, a modified process design was made for both the fluid bed and dispersed phase schemes and ultimately, because of favorable economics, the design without the solids cooler was selected as the base case.

Elimination of the solids cooler resulted in 1400°F solids being fed directly into the reactor and required that an evaluation of the effect, if any, on reactor design be made. In the fluid bed case, no changes to the reactor were necessary because of the rapid heat transfer obtained in a fluid bed; i.e., the hot solids fed into the reactor are cooled to the equilibrium bed temperature almost instantaneously and no extra height for heat transfer is needed. The dispersed phase case reactor did require modification, however, since very few sorption data were available at high temperatures and to insure an adequate reactor

design it was assumed that sorption would not occur until the solids had been cooled to the equilibrium temperature. It was further assumed that the sorption rates would not change because of the new equilibrium temperatures which are increased from the original value of 600°F to 634°F and 658°F for the fluid bed and dispersed phase cases respectively. The higher temperatures both cases are a result of cooling the sorbent with the flue gas which enters the system at 600°F, and the higher dispersed phase equilibrium temperature is due to the difference in solids throughput.

In addition to the increased height of the dispersed phase reactor other changes resulting from eliminating the solids cooler are a smaller air compressor, and deletion of the after-cooler and water knockout drum. The heat balance around the solids heater is also affected since the solids enter at a higher temperature and preheated air is no longer available. The effect of these revisions was a net reduction in investment and operating costs and resulted in the designs without the solids cooler being selected for the base cases. Investment and operating costs are discussed in following sections C and D. respectively. The methods used in calculating the new dispersed phase reactor height are discussed below. Also presented is a sample calculation for the reactor height.

The increase in reactor height is determined by the time it takes for the 600°F flue gas and 1400°F sorbent particles to reach the equilibrium temperature of 658°F. Various methods were used to calculate the equilibrium time as follows:

- Bird, R. B., Stewart, W. E., Lightfoot, E. N., TRANSPORT PHENOMENA, Wiley & Sons, Inc., New York, 1960, p. 357-360.

This method involves the use of a plot indicating the variation of fluid temperature with time when a homogeneous sphere of solid material, initially at a uniform temperature, is suddenly immersed in a well-stirred

fluid, at another temperature in an insulated tank. The temperature distribution in a sphere resulting from unsteady-state heat conduction can be predicted since the necessary mathematical equations are solved and the results presented in graphical form. This procedure considers the sphere surface to be suddenly raised to the fluid temperature at initial time zero and predicts the temperature distribution then obtained with increasing time.

- McAdams, W. H., HEAT TRANSMISSION, 3rd ed., McGraw-Hill Book Co., Inc., New York, 1954, p. 40

Graphical solutions of the equations for the transient heating or cooling of a sphere are presented. The relations between temperature and time for various points along a radius can be obtained from the Gurney-Lurie chart for spheres. These relations involve the thermal conductivity, density, and specific heat of the body, its shape and size, and the external conditions, including the temperature of the surroundings and the coefficient of heat transfer between surroundings and the surface.

- Particle Heat Balance

The heat evolved in decreasing the temperature of the particle must be equal to that determined from an overall heat requirement, namely the product of three parameters: the fluid-particle heat transfer coefficient, the area of the particle, and the log-mean temperature driving force.

In eliminating the solids cooler in the dispersed phase case, the optimum condition would be for the solids to cool from their entering temperature of 1355°F to the equilibrium temperature of 658°F in a relatively short time so that any additional required

sorber height would be kept at a minimum. Assuming that the lighter particles are not recycled, sufficient height must be provided in the sorber such that they can be cooled down in one pass since the heavy particles will be recycled. To determine which particle size would require the greatest height, and thus set the design, calculations were made for several different size particles, using the size distribution obtained from an attrition run reported in the Bruceton Quarterly of 12-31-67 (see Figure 5, this report). A sample calculation of the time required for equilibrium to be reached in the dispersed phase sorber for a 1410 micron particle diameter is included as Appendix K. A summary of the additional sorber height required for the attainment of the proper equilibrium temperature, for various particle sizes, is included as Table 46.

Values of thermal conductivity for alkalized alumina were not available, so alumina (Al_2O_3) values were used instead. Different values of thermal conductivities are reported in the literature for Al_2O_3 , however, so two values (0.392 and 0.087 Btu/hr-ft) were used in these calculations. For the 1410 micron diameter particle, which, as shown in Table 46, sets the additional sorber height required, the results came out quite similar, namely 36 and 38 feet using the Gurney-Lurie chart for spheres. These heights are in good agreement with the value of 29 feet as calculated by a partial heat balance. Both these methods yielded a considerably greater height than that predicted using the method of Bird, Stewart and Lightfoot but this is probably due to the fact that the latter approach assumes the surface of the sphere to be instantaneously adjusted to the fluid temperature. As a result of these calculations, it was decided that the dispersed phase sorber should be 35 feet higher for the case of operation without a solids cooler. Therefore, the previously calculated reaction height of 80 feet was increased by 35 feet and another 10 feet was added to allow for gas distribution baffles such that a "reaction zone" height of 125 feet was obtained. A sketch of the final design of the dispersed phase sorber is shown in Figure G-93.

TABLE 11

HEIGHT REQUIRED FOR PARTICLE-GAS HEAT
DISPERSED PHASE REACTOR - 1000MW POWER

SOLIDS: 1330 + 658°F
GAS: 600 + 658°F

PARTICLE SIZE			SLIP VELOCITY	FLUID TO PARTICLE HEAT TRANSFER COEFFICIENT*	SOLID THERMAL CONDUCTIVITY	CALCULATED
(MESH)	(MICRONS)	(FT)	$(\bar{V}_{\text{gas}} - \bar{V}_{\text{set. vel.}})$ (ft/sec)	h (Btu/hr/ft ² F)	K_s (Btu/hr/ft F)	1††
8	2362	0.00776	-9.5	22.2	0.392** 0.087†	0.9 3.9
10	1651	0.00542	-1	8.2	0.392 0.087	0.42 1.9
-10+14	1410 _{av}	0.00462 _{av}	+3	15.6	0.392 0.087	0.31 1.4
60	246	0.00080	+22.1	102.3	0.392 0.087	0.009 0.04

- * h calculated - Treybal, R. E., Mass Transfer Operations, McGraw-Hill Book Co.
 ** k_s Al₂O₃ from Lange, N. A., Handbook of Chemistry, revised 10th ed., McGraw-Hill.
 † k_s Al₂O₃ from Thermophysical Properties Research Center, Data Book, Purdue U.
 †† Bird, R. B., Stewart, W. E., and Lightfoot, E. N., TRANSPORT PHENOMENA, Wiley.
 ††† McAdams, W. H., HEAT TRANSMISSION, 3rd ed., McGraw-Hill Book Co., Inc., New York.

- 1 - Bird, Stewart, Lightfoot Method
 2 - Gurney-Lurie, Chart for Spheres
 3 - Particle Heat Balance

A

TABLE 11

T REQUIRED FOR PARTICLE-GAS HEAT TRANSFER

ERSED PHASE REACTOR - 1000MW POWER PLANT

SOLIDS: 1330 + 658°F

GAS: 600 + 658°F

ID TO TICLE TRANSFER FICIENT*	SOLID THERMAL CONDUCTIVITY K _s (Btu/hr/ft F)	CALCULATED EQUILIBRIUM TIMES			REQUIRED EQUILIBRIUM HEIGHT		
		(SECONDS)			(FT)		
h (hr/ft ² F)		1++	2+++	3	1	2	3
22.2	0.392**	0.9	14	11.4	9.	133	108
	0.087+	3.9	18	--	37.	171	-
8.2	0.392	0.42	30	21.6	0.4	30	22
	0.087	1.9	26		1.9	26	
15.6	0.392	0.31	12	9.7	1.	36	29
	0.087	1.4	12.5		4.	38	
02.3	0.392	0.009	0.32	0.29	0.2	7	6.5
	0.087	0.04	0.33		0.9	7.5	

er Operations, McGraw-Hill Book Co., Inc., New York, 1955, p. 54 - Curve 4.

emistry, revised 10th ed., McGraw-Hill Book Co., Inc., New York, 1963.

search Center, Data Book, Purdue University, Lafayette, Indiana, 1964.

, E. N., TRANSPORT PHENOMENA, Wiley & Sons, Inc., New York, 1960, p. 360, Fig. 11.1-4.

, McGraw-Hill Book Co., Inc., New York, 1954, p. 40-Fig. 3-7.

B

C. INVESTMENT

Estimates have been completed for the entire battery limits plant (i.e., excluding offsites) for each of the three processes and the investments, including the initial charge of sorbent, are: dispersed phase - \$30,720,000; fluid bed - \$35,900,000; and fixed bed - \$40,210,000. A breakdown of the investments into major items is shown in Table 47 including a tabulation of the material and subcontract costs of the major items. Accuracy of the investments, based on the current flow sheets, is in the range of -5% to +25%.

The cost of the sorption-regeneration section in each case includes that equipment as shown on the individual flow sheets for each design while the regeneration gas plant investment shown in Table 47 is the total installed cost based on the flow sheet described in section B.2.e.(1) (Figure 57).

The total installed cost of the Claus plant pretreatment section is \$810,000 for the fixed bed design, based on the discussion and flow sheet described in section B.2.e.(2) (Figure 58), and is \$100,000 for the fluid bed and dispersed phase designs. The only equipment required for the latter two designs is a waste heat boiler.

The total erected cost of the Claus plant and incinerator, (Section B.2.e.(3)) including the waste heat boiler, sulfur pumps, etc., is \$1,500,000 for the fixed bed design and \$1,400,000 for the fluid bed and dispersed phase cases. The slightly higher cost for the fixed bed unit is due to the increased sulfur removal obtained in the fixed bed sorbers, hence the Claus plant is correspondingly larger. The Claus feed gas from the fixed bed design has a higher concentration of H_2S than the fluid bed or dispersed phase and this partially offsets the cost due to the larger size but the net result is an increase in cost for

TABLE 47

APPROXIMATE DISTRIBUTION OF PROCESS INVESTMENT-BATTERY LIMITS PLANT

ITEM	DOLLARS		
	DISPERSED PHASE	FLUID BED	FIXED BED
1. Sorption-Regeneration*			
Converters	12,200,000	13,600,000	11,600,000
Fans & Compressors	1,300,000	2,500,000	2,800,000
Large Valves (Gas Duct)	-	-	6,200,000
Ducts & Piping	8,300,000	10,900,000	9,900,000
Other	300,000	630,000	480,000
Sub-total (1)	22,100,000	27,630,000	30,980,000
2. Regeneration Gas Plant	3,300,000	3,300,000	**3,300,000
3. Claus Gas Pretreatment	100,000	100,000	810,000
4. Claus Plant, including incinerator	1,400,000	1,400,000	1,500,000
5. Δ Cost Electrostatic Precipitator	2,870,000	2,870,000	2,870,000
6. Δ Cost Air Preheater	400,000	200,000	260,000
Sub-total (1+5)	30,170,000	35,500,000	39,720,000
7. Sorbent Inventory (@ 25¢/lb)	550,000	400,000	490,000
Total	30,720,000	35,900,000	40,210,000

* See next page for material cost breakdown.

** Fixed bed requires about 10% higher capacity and lower temperature than other two cases but investment shown does not include allowance for this difference. Added cost for higher capacity would be about \$250,000.

TABLE 47 (CON'T)

MATERIAL & SUBCONTRACT COST, DOLLARS			
ITEM	DISPERSED PHASE	FLUID BED	FIXED BED
<u>Vessels</u>			
Reactors	1,077,200	3,693,000	
Reactor Cyclones	2,640,000	1,730,000	
Gas-Solids Separators	42,000	41,600	
Solids Heaters	187,400	149,000	4,200,000
Regenerators	557,400	189,800	
Sorbent Storage Hopper	19,000	19,000	
Recycle Flue Gas Heater	-	-	125,000
<u>Fans & Compressors W/Motors</u>			
Air Compressors	395,000	265,000	
I.D. Fans (Increment)	228,000	988,000	-
Recycle Gas Blowers	-	-	968,000
Air Blowers	-	-	75,000
Claus Gas Compressors	-	-	15,000
			300,000
<u>Piping</u>			
Flue Gas Ducts & Expansion Joints	1,200,000	1,800,000	2,450,000
Air Ducts (Incremental)	800,000	800,000	800,000
Other Piping & Valves	900,000	1,340,000	300,000
Duct Valves	-	-	2,750,000
Total Major Material	8,046,000	11,015,400	11,983,000

the fixed bed Claus plant.

All three alkalized alumina processes result in a larger electrostatic precipitator being required by the power plant. The reasons for the increased size were cited earlier (section B.2.C.(4)) and, very briefly are: increased gas volume because of a higher temperature for the fixed and fluid bed designs, and lowered efficiency in the dispersed phase case. The incremental size, hence cost, of the precipitator is directly caused by, and therefore charged to, the alkalized alumina process. In all three cases, the total incremental cost including additional piping, ductwork foundations, etc. is estimated to be \$2,870,000. The basic equipment cost was obtained from a vendor and the total installed cost was estimated by Kellogg.

The cost of the power plant air preheater is increased by the alkalized alumina plant owing to the higher temperature and flow rate of the exit gas. The incremental cost of the air preheater is included as part of the alkalized alumina plant investment. The material cost of this item for each case was obtained from a vendor and the total installed cost was estimated by Kellogg to be \$400,000, \$200,000, and \$260,000 for the dispersed phase, fluid bed, and fixed bed designs respectively.

It should be noted that a major item in all three designs is ducts and piping, comprising about 70-80% of the reactor cost in all three cases. Thus it is apparent that total investment obtained through the use of normal scale-up factors and cost of major equipment would likely be substantially lower than the actual cost because the full effect of the very costly ductwork would not be obtained. If it is desired to determine total plant investment from the major equipment cost, it is essential that the large ductwork be included as a major equipment if reasonably realistic results are to be obtained.

The approximate quantity of large ductwork and piping required for each process was obtained from the rough layout prepared for each design. Since the ductwork and piping comprise such a large percentage of the total investment (i.e., ~30%), it is essential to have at least an approximate plant layout from which the amount of ductwork can be estimated. Without a plant layout the quantity, hence cost, of the large ductwork can be substantially in error which in turn would result in a plant investment that is probably too low.

The major equipment items were designed in sufficient detail to insure process and mechanical feasibility, and cost estimates for the individual items were obtained from outside vendors when ever practical. When vendor quotes could not be obtained, estimates were made by MWK. In the fixed bed case, the large valves were designed and estimated specifically for this process by the Grove Valve & Regulator Company, after approximate specifications were jointly developed with MWK. The present status is a preliminary design of a retracted disc valve which appears to be suitable for the process conditions involved.

D. ECONOMICS

1. Base Case

a. Gross Costs

Based on the complete plant investments shown in Section C and a load factor of 60% (5250 hours/year), process economics have been calculated for each case and are summarized in Table 48. A tabulation of the individual items for the dispersed phase, fluid bed and fixed bed designs is shown in Tables 49, 50, and 51 respectively. It should be noted that the costs shown in Tables 48 through 51 do not include sorbent attrition losses or credit for by-product sulfur.

The values used for the individual items shown in Tables 49, 50, and 51, are essentially those listed in a report obtained from NAPCA (1). The NAPCA recommended guide lines agree quite closely with MWK recommendations derived from a study of various sources (2 thru 7).

1. NAPCA, "General Guide-Lines for the Process Economic Evaluation of the Nine-Area Surveys for SO₂ Removal".
2. Office of Saline Water, "A Standardized Procedure for Estimating Costs of Saline Water Conversion," March 1956.
3. The M. W. Kellogg Company, Report RED-68-1173 to the office of Coal Research, Contract No. 14-01-0001-380, September 1, 1968, p. 123.
4. The M. W. Kellogg Company, Report RD-62-952 to the U. S. Atomic Energy Commission, Contract No. AT (30-1)-3009 (NYO 10,301), November 30, 1962, p. 167.
5. Aries, R. S. and R. D. Newton, "Chemical Engineering Cost Estimation," McGraw Hill Book Company, Inc., New York, 1955, pp. 162-182.
6. Peters, M. S. "Plant Design and Economics for Chemical Engineers," McGraw-Hill Book Company, Inc., New York, 1968, pp. 108-9, 113.

TABLE 48

ANNUAL COSTS - BASE CASE

(EXCLUDING ATTRITION LOSSES AND SULFUR CREDIT)

ITEM	DOLLARS/YR	
	DISPERSED PHASE	FLUID BED
1. Capital Charges	3,993,600	4,667,000
2. Labor, Maintenance, and Overhead	2,889,300	3,396,200
3. Utilities	991,100	1,271,500
TOTAL	7,874,000	9,334,700
		5,227,300
		3,767,900
		1,433,300
		10,428,500

Unit Costs

mills/kwh	1.50	1.78	1.99
¢/MM Btu	17.42	20.67	23.10
/ton coal	4.53	5.38	6.01

NOTE: Coal used in design contains 13,000 Btu/# and costs 25¢/MM Btu (\$6.50/ton).

TABLE 49

DISPERSED PHASE - PROCESS ECONOMICS

<u>DIRECT COST</u>	<u>\$/YEAR</u>
1. Operating Labor (4 men/shift @ \$3.50/hr)	\$ 122,600
2. Supervision - 15% of labor	18,400
3. Maintenance @ 5% °F FCI	1,536,000
4. Supplies - 15% of (3)	230,400
5. Utilities: a. Cooling Water @ 5¢/M gal.	79,100
b. Natural Gas @ 27¢/MM Btu	921,000
c. Power @ 0.6¢/kwh	385,400
6. Heat (credit) @ 25¢/MM Btu	(293,000)
7. Steam (credit) @ 25¢/M lbs	(101,500)
8. Total Direct Cost	\$2,898,500
<u>INDIRECT COST</u>	
9. Payroll Overhead - 20% of (1 + 2)	\$ 28,200
10. Plant Overhead - 50% of (1 + 2 + 3 + 4 + 5)	953,700
11. Total Indirect Cost	\$ 981,900
<u>FIXED COST</u>	
12. Capital Charges @ 13% °F FCI (Depreciation, insurance, taxes, cost of capital, etc.)	\$ 3,993,600
13. TOTAL OPERATING COST (8 + 11 + 12)	\$ 7,874,000
<u>UNIT COSTS</u>	
14. a. \$/ton coal	4.53
b. ¢/MM Btu in coal feed	17.42
c. Mills/kwh	1.50

- Notes: 1. No credit taken for by-product sulfur which is produced at rate of 46,870 short tons/year.
2. Power plant operates at full capacity 60% of time or 5250 hours/year.
3. Costs do not include attrition loss.

FCI = Fixed Capital Investment = \$30,720,000

TABLE 50

FLUID BED - PROCESS ECONOMICS

<u>DIRECT COST</u>	<u>\$/YEAR</u>
1. Operating Labor (5 men/shift @ \$3.50/hr)	153,300
2. Supervision - 15% of labor	23,000
3. Maintenance @ 15% of FCI	1,795,000
4. Supplies - 15% of (3)	269,300
5. Utilities: a. Cooling Water @ 5¢/M gal.	79,100
b. Natural Gas @ 27¢/MM Btu	808,700
c. Power @ 0.6¢/kwh	686,200
6. Heat (credit) @ 25¢/MM Btu	(201,000)
7. Steam (credit) @ 25¢/M lbs	(101,500)
8. Total Direct Cost	\$3,512,100
<u>INDIRECT COST</u>	
9. Payroll Overhead - 20% of (1 + 2)	35,300
10. Plant Overhead - 50% of (1 + 2 + 3 + 4 + 5)	1,120,300
11. Total Indirect Cost	1,155,600
<u>FIXED COST</u>	
12. Capital Charges @ 13% ^o F FCI (Depreciation, insurance, taxes, cost of capital, etc.)	4,667,000
13. TOTAL OPERATING COST (8 + 11 + 12)	9,334,700
<u>UNIT COST</u>	
14. a. \$/ton coal	5.38
b. ¢/MM Btu in coal feed	20.67
c. Mills/kwh	1.78

- NOTES: 1. No credit taken for by-product sulfur which is produced at rate of 46,870 short tons/yr.
 2. Power plant operates at full capacity 60% of time or 5250 hours/year.
 3. Costs do not include attrition loss.

FCI - Fixed Capital Investment = \$35,900,000

TABLE 51

FIXED BED - PROCESS ECONOMICS

<u>DIRECT COST</u>	<u>\$/YEAR</u>
1. Operating Labor (5 men/shift @ \$3.50/hr)	153,300
2. Supervision - 15% of labor	23,000
3. Maintenance @ 5% of FCI	2,010,500
4. Supplies - 15% of (3)	301,600
5. Utilities: a. Cooling Water @ 5¢/M gal.	138,200
b. Natural Gas @ 27¢/MM Btu	876,400
c. Power @ 0.6¢/kwh	698,600
6. Heat (credit) @ 25¢/MM Btu	(169,500)
7. Steam (credit) @ 25¢/M lbs	(110,400)
8. Total Direct Cost	3,921,700
<u>INDIRECT COST</u>	
9. Payroll Overhead - 20% of (1 + 2)	35,300
10. Plant Overhead - 50% of (1 + 2 + 3 + 4 + 5)	1,244,200
11. Total Indirect Cost	1,279,500
<u>FIXED COST</u>	
12. Capital Charges @ 13% °F FCI (Depreciation, insurance, taxes, cost of capital, etc)	5,227,300
13. TOTAL OPERATING COST (8 + 11 + 12)	10,428,500
<u>UNIT COST</u>	
14. a. \$/ton coal	6.01
b. \$/MM Btu in coal feed	23.10
c. Mills/kwh	1.99

- Notes: 1. No credit taken for by-product sulfur which is produced at rate of 50,370 short tons/yr.
 2. Power plant operates at full capacity 60% of time or 5250 hrs/yr.
 3. Costs do not include attrition loss.

FCI = Fixed Cost Investment = \$40,210,000

7. Letter from C. W. Carry, Los Angeles County Sanitation Districts to A. N. Massi, Federal Water Pollution Control Administration, October 31, 1968.

Referring to Tables 49, 50, and 51, the operating labor includes two men per shift for the reformer and Claus plant associated with each process. The number of operators required for the reformer and Claus plant was derived from Kellogg's experience with reformers for ammonia plants and is believed to be a realistic estimate. However, it should be noted that the total annual cost of the operating labor is small compared to the overall cost of the complete plant so even an error of 100% in the estimate of the number of operators required will not have a significant effect on process economics. It is assumed that any additional labor required for start-up will be available from the power plant operating staff. Supervision, maintenance, supplies, overhead, and capital charges are calculated as indicated in Tables 49, 50, and 51.

The base case economics include an annual maintenance cost of 5% of fixed capital investment (FCI). It should be noted that calculating maintenance as a percentage of FCI is a standard procedure by many companies, especially those which use contract maintenance. The annual maintenance costs typically vary with plant life, being higher at the beginning, decreasing, and then increasing. Two examples of maintenance costs based on actual plant experience are:

- 1) The average maintenance charges for the first 10 years of a low-overhead chemical plant are about 4.5% of FCI, ranging from a high of about 8% to a low of 3.0%,
- 2) The average maintenance costs of a complete refinery are about 4% of FCI. It should be noted that these values are

for well established, proven processes as opposed to a new design such as the alkalized alumina. Since the large-sized ductwork comprises a significant portion of the alkalized alumina plant investment, possibly lower maintenance costs could be used. Because of the different operating conditions (i.e., higher temperature, higher pressure, longer runs), of the alkalized alumina plant ductwork compared to that normally encountered in a power plant, however, it is felt that the maintenance costs will be higher than normal. For example, the maintenance requirements for the large expansion joints in the large diameter ducts are not well defined; painting of the ducts will also be required on some regular basis and owing to the quantities involved, this could be a major item.

Another point to consider is the local conditions at any given site; i.e., contract maintenance may not be available, or if internal maintenance is used, certain crafts may be required that are not available from the power plant maintenance force. Thus, depending on the local labor union situation, it might be necessary to carry several different crafts on the payroll even though they are not needed full time.

To summarize, the base case economics include annual maintenance costs of 5% of FCI as compared to 4 to 4-1/2% for well established processes and because of the various qualifying factors discussed above, it is felt that the 5% charge is a reasonable value. To account for other possibilities, however, the effect of different maintenance charges on process economics will be studied on part of the phase 3 evaluation.

The utilities shown are for a battery limits plant, including heat and steam credits. It is assumed that all flue gas streams (e.g., from reformer, Claus incinerator)

will be mixed with the main flue gas stream at locations upstream of the power plant air preheater. Using an exit flue gas temperature of 300°F (i.e., downstream of the air preheater) the heat available from the various flue gas streams above 300°F has been calculated and credited to the alkalized alumina process. Since the total volume of the gas flowing through the air preheater is increased by adding these additional streams, an incremental cost has been added to allow for the increase in the size of the air preheater.

Credit has also been taken for excess steam generated by the alkalized alumina process. Most of the steam can be used internally (e.g., steam-reformer, steam drive on the Claus plant air blower) and the excess can be used either in the power plant circuit or in the alkalized alumina process itself if steam drives are used on the booster fans. In either case, a credit can be taken for the excess steam and a value equal to the coal cost has been assumed. Possibly, a higher steam value could be used but the total steam credit is small and does not significantly affect process economics, and therefore, the value used is considered adequate for the present evaluation.

The capital charge rate used in the base case economics is 13% nominally based on NAPCA guide lines comprising 10% straight line depreciation and 3% for taxes and insurance. Since the total capital charge rate, not the individual items, is the important factor, and since this rate usually falls between 13 and 16% of original investment for power plants, the lower value was selected because it agreed with the NAPCA figure. It is recognized that using a 10 year straight line depreciation and adding appropriate values for taxes, insurance, and cost of money would result in a higher

capital charge rate. In fact, TVA has presented an example¹ wherein a 35 year plant life was used and the annual charges - levelized basis were calculated to be 14.5%. Thus the value of 13% may be low in view of the fact that the alkalized alumina plant life would be less than the 35 years expected for the power plant. However, the lower value was used in keeping with the general rationale of taking an optimistic approach whenever possible.

As was also pointed out by TVA² installing a sulfur removal process as part of a power plant leads to complications because of the differences in the two industries involved; i.e., the regulated power company or the free enterprise chemical company. Three different investment approaches for air pollution control facilities are cited by TVA, viz: 1) all power company investment; 2) all chemical company investment; 3) mixed investment venture. Each of these three methods including variations would require a different method of calculating costs. Since a detailed analysis of power plant costing methods was beyond the scope of this study, the simplified approach of using an average capital charge rate based on original investment was selected. It is recognized that the 13% rate selected is probably low in view of the above discussion, but in the present case the plant costs are so high that adding additional costs owing to a higher capital charge rate seemed superfluous.

As previously noted, the economics presented herein, are based on a load factor of 60% (5250 hours/year). The rationale used in arriving at this value is given below.

Normally, as large-size, more efficient plants come on stream they are base loaded and thus run at a higher stream efficiency than older, less efficient units. However, since the trend in power plants appears to be toward larger units,

¹ SULFUR OXIDE REMOVAL from power plant stack gas
Prepared by Tennessee Valley Authority for Second Semiannual
Control Process Contractors' Meeting, National Air Pollution
Control Administration, Cincinnati, Ohio, June 11-13, 1969, p. 18.

² Ibid, pp. 29-30.

and with the installed generating capacity expected to double about every 10 years, it would seem that at some future time most of the power plants will be large units. Therefore, as long as there is a large difference between peak and off-peak power demands, and if most of the units are large-sized, then some of the large-sized plants will have to be shut down and their load factor will not be as high as if only a few large plants existed. It should also be noted that the net heat rates for large plants has been leveling off over the past few years (Federal Power Commission, National Power Survey-Part I", Washington, D. C., 1964) and thus the difference in thermal efficiency between large plants built after about 1960 is relatively small. Thus, in the future the load factor of the older plants will approach that of the newer ones and both will approach that of the entire system.

TVA¹ have presented a suggested time-load factor ranging from 80% for the first 10 years down to 17% for the last 15 years. The overall average for a 35 year power plant line is 44% based on the TVA numbers, with the first 20 years averaging about 64%. The life of the plant therefore is an important factor in setting the load factor.

Information was also obtained from Consolidated Edison Co., NYC, and Commonwealth Edison, Chicago, and these sources suggested that a 60% load factor was too high and, in fact, a value of about 55% would be better. This latter figure also agrees with the results of a survey made for NAPCA by Battelle Memorial Institute. However, it was subsequently decided to use the 60% value to calculate the base case costs.

Finally, it is very unlikely that the identical stream efficiency will apply to all locations. The present

¹ Ibid, p. 28.

design is for a general case, however, and an average value must be used. Based on the information available and the rationale presented above, a 60% load factor was selected as being a reasonable value to use in the economics analysis. Further, because of the uncertainty as to what the actual load factor might be at the time and for the location at which a sulfur oxides removal plant is installed, a separate study of the effect of load factor on plant economics will be made in the phase 3 work.

Total annual operating costs and unit costs have been calculated for each case and are shown in Tables 49, 50, and 51. Based on the values shown it can be seen that the alkalized alumina process will add about 76% to 92% to the fuel cost when burning a 13,000 Btu/lb coal at 25 cents per million Btu (\$6.50/ton). These are the gross costs and do not include attrition losses or sulfur credit, whose effects are discussed later. Two major reasons for the high costs are the high capital investment required and the low load factor of the power plant. Possibly the power plant would operate at a higher load factor during the first 10 years of its life, the assumed life of the alkalized alumina plant, which would decrease the unit costs. On the other hand, the capital charges used (13%) may be too low as discussed above, and higher rates would of course, increase costs. A study of the effect of capital charges, load factor, and depreciation period is planned for the Phase 3 study and, therefore, only the base case is used in the present design.

b. Net Costs

The effect of attrition losses and by-product sulfur credit is shown in Table 52. An assumed attrition rate is used for each process as follows: 0.1% of the solids throughput for the dispersed phase case, one half this rate (0.05%)

TABLE 52

PROCESS ECONOMICS INCLUDING ATTRITION LOSSES

AND

BY-PRODUCT SULFUR CREDIT

Basis: Sorbent @ 25¢/lb
Sulfur @ \$20/ton

	<u>DISPERSED PHASE</u>	<u>FLUID BED</u>	<u>FIXED BED</u>
Assumed Attrition Loss, lb/yr	3,706,500	997,500	633,500

DOLLARS/YEAR

ANNUAL COSTS

Cost of Sorbent
Credit, by-product Sulfur
Gross Cost (Tables 49, 50, 51)
Net Cost

926,600	249,400	158,400
(937,400)	(937,400)	(1,007,400)
7,874,000	9,334,700	10,428,500
7,863,200	8,646,700	9,579,500

UNIT COSTS

¢/MM Btu in coal feed
\$/ton coal
Mills/kwh

17.42	19.15	21.22
4.53	4.98	5.52
1.50	1.65	1.82

for the fluid bed design, and fixed bed sorbent life of twice the fluid bed life based on the number of sorption-regeneration cycles. It is expected that the dispersed phase attrition will be the highest since the highest gas velocity is used in this process; similarly, the attrition in the fixed bed should be the lowest since it uses the lowest gas velocity, and, in addition, does not require the transfer of solids between sorber and regenerator. The fluid bed attrition will probably fall in between these two. The absolute values used, however, are purely arbitrary since actual attrition data are not presently available. The unit price of make-up sorbent is assumed to be 25 cents per pound.

Credit for by-product sulfur is calculated from the annual tonnage produced by each process assuming a net price of \$20 per ton will be obtained. The term "net price" for sulfur as used here is defined as the sulfur selling price less all costs associated with producing and selling the sulfur, including handling, storage, distribution, sales expenses, etc. Basis for the selection of a \$20/ton selling price for the by-product sulfur produced by the alkalized alumina plant is discussed below.

The competition for sulfur markets would be from the existing sulfur producers and since the cost of producing Frasch sulfur is in the order of \$10 per ton it seems apparent that sulfur prices above \$20 per ton are unlikely. It should be noted that historically the sulfur selling price has fluctuated over a wide range as the supply and demand relationship changed. From the changes in sulfur price that have occurred over the past few years (i.e., ~\$20/ton), it would appear that the sulfur producers have the capability of making money at prices in the \$20/ton range. While the 40,000 to 50,000 tons per year of sulfur output from a single power plant probably would not cause any great effect on sulfur price, it does seem most likely that if enough of these plants were built such that their

sulfur output was a significant portion of the market, then the price of sulfur would probably drop to the \$20 per ton range. As a point of interest, it should be noted that sulfur recovered from natural gas is presently (first quarter 1970) being sold for less than \$15 per short ton.

Since the price for which by-product sulfur can be sold does not appear to be clearly established at the present time, the effect of different sulfur prices on process economics will be evaluated in our phase 3 work. Sulfur prices ranging from \$0 to \$40 per ton will be used and the effect on process economics determined.

Comparing the results in Table 52, which are based on a sulfur net selling price of \$20/ton, with those in Tables 49, 50, and 51 shows that a net reduction in cost is obtained only in the fixed and fluid bed cases, with the dispersed phase case cost remaining essentially unchanged. Further, the amount of reduction obtained is only about 9% and therefore does not greatly improve the overall economics.

As can be seen from Table 52, the total annual revenue from the sale of by-product sulfur is only about \$1,000,000. The sulfur credit is limited by the relatively low price and the small quantities produced. The sulfur selling price that can reasonably be expected under normal competitive conditions will most likely be less than the list price since the sulfur is a by-product, and the quantities are limited by the sulfur content of the coal burned and the low load factor of the power plant. Comparing the sulfur credit with the sorbent attrition cost shows credit to cost ratios of about 1:1, 4:1, and 6:1 for the dispersed phase, fluid bed, and fixed bed cases respectively. Thus, the assumed attrition losses can be in error by a factor of 6 for the fixed bed and a factor of 4 for the fluid bed

without increasing the process costs shown in Tables 50 and 51. Any increase in dispersed phase attrition losses, however, will cause an increase in the process costs shown in Table 49. In fact, if the dispersed phase attrition losses are doubled (0.2% instead of 0.1%, basis solids throughput), the net annual costs of the dispersed phase and fluid bed designs become about the same. Since the attrition losses are assumed, and since the dispersed phase losses are the highest and probably the most likely to be in error, the sensitivity of dispersed phase economics to attrition losses precludes any firm conclusion that the dispersed phase design offers the lowest costs. Once a suitable sorbent is developed and long term steady state data are obtained, a more exact comparison of the three processes can be made.

2. Final Process Design

The original design of the dispersed phase and fluid bed processes included a solids cooler in both cases. As an alternative design, the solids cooler was eliminated and the changes in process investment and operating costs were calculated. Table 53 summarizes the reduction in total investment for both the dispersed phase and fluid bed schemes when the solids cooler is removed. There is a decrease in total investment of about \$1,800,000 and \$1,300,000 for the dispersed phase and fluid bed cases respectively. It should be noted that these values are independent of sorbent inventory, Claus plant, reducing gas generator, and the incremental cost of the power plant electrostatic precipitator, and therefore can be applied directly to the base case plant investment. The savings in investment and process economics for the dispersed phase and fluid bed cases owing to deletion of the solids cooler have been summarized in Tables 54 and 55.

TABLE 53

TOTAL INVESTMENT DECREASE FROM REMOVAL OF THE SOLIDS COOLER
(DISPERSED PHASE AND FLUID BED SCHEMES)

EQUIPMENT ALTERNATION FROM ORIGINAL FLOW SHEETS	DOLLARS			
	DISPERSED PHASE		FLUID BED	
	MATERIAL	SUBCONTRACT	MATERIAL	SUBCONTRACT
Compressor Aftercoolers Removed	-80,000	-	-48,000	-
Absorber Heights Increased	+90,000	+47,200	-	-
Solids Coolers Removed	-140,400	-364,400	-78,800	-260,000
Water Knock-out Drums Removed	-	-58,800	-32,000	-
Inlet Air Compressor Decrease in Capacity	-385,000	-	-175,000	-
Change in Process Equipment	-515,400	-376,000	-333,000	-260,000
Material and Subcontract Cost				
Change in Total Investment	1,840,000		1,290,000	

TABLE 54

CHANGE IN PROCESS ECONOMICS FROM DELETION OF SOLIDS COOLER

DISPERSED PHASE

(EXCLUDES ATTRITION LOSS AND SULFUR CREDIT)*

	<u>CHANGE (DECREASE)</u>
Fixed Capital Investment (\$):	1,840,000 (~5.7%)
<u>Annual Operating Costs (\$/yr):</u>	
Capital Charges	240,000
Labor, Maintenance, and Overhead	150,000
Utilities	580,000
TOTAL	970,000 (~11%)
<u>Unit Costs:</u>	
\$/ton coal	0.56
¢/MM Btu	2.1
Mills/kwh	0.18

* By-product sulfur produced at rate of 46,870 short tons/year.
Power plant at full capacity 60% of time or 5250 hours/year.

Note: Coal used in design contains 13,000 Btu/lb and costs
25¢/MM Btu (\$6.50/ton).

TABLE 55

CHANGES IN PROCESS ECONOMICS FROM DELETION OF SOLIDS COOLER

FLUID BED

(EXCLUDES ATTRITION LOSS AND SULFUR CREDIT)*

<u>ITEM</u>	<u>CHANGE (DECREASE)</u>
Fixed Capital Investment (\$):	1,290,000 (~3.5%)
<u>Annual Operating Costs (\$/yr):</u>	
Capital Charges	170,000
Labor, Maintenance, and Overhead	120,000
Utilities	220,000
TOTAL	510,000 (~5.6%)
<u>Unit Costs:</u>	
\$/ton coal	0.29
¢/MM Btu	1.1
Mills/kwh	0.097

* By-product sulfur produced at rate of 46,870 short tons/year.
Power plant at full capacity 60% of time or 5250 hours/year.

Note: Coal used in design contains 13,000 Btu/lb and costs 25¢/MM Btu (\$6.50/ton).

As can be seen from Tables 54 and 55, elimination of the solids cooler results in an overall reduction in costs for both cases. The reduction in gross annual cost is about \$970,000 for the dispersed phase plant and about \$510,000 for the fluid bed plant, which are equivalent to unit cost reductions of \$0.56 per ton of coal (2.1¢/MM Btu, 0.2 mills/kwh), and \$0.29 per ton of coal (1.1¢/MM Btu, 0.1 mills/kwh), respectively. Based on these results it was decided to use the process scheme from which the solids cooler had been eliminated as the base case for both the dispersed phase and fluid bed designs. Therefore, the investments and operating costs shown earlier in this report are for the designs in which the solids cooler has been eliminated.

If the assumptions upon which these designs and economics are based are correct, then it appears that the dispersed phase design offers the best economics of the three processes studied. The absolute level of cost is still high, however, since the best case (dispersed phase) shows an increase in fuel cost of about 70% (i.e., \$4.53/ton increase on the base cost of \$6.50/ton). In addition, if some of the assumptions are changed (e.g., relative attrition rates of the three designs), the advantage indicated above for the dispersed phase case could be lost.

APPENDIX A

ATTRITION TEST METHODS

1. Introduction

A summary is presented of the different attrition test methods used by various investigators to measure attrition losses of alkalized alumina. Also included is a copy of Cyanamids' test methods which are based on the Standard Oil Company (Indiana) method used by Forsythe and Hertwig, IEC, 41, 1200(1949). A copy of the latter method is also included.

- a. Figure 59 depicts the USBM pneumatic conveyor attriter which is discussed in Section A. 1. a.(1) of this report.
- b. The accelerated air-jet attrition (AAJA) test for alkalized alumina developed by W. R. Grace and Company. This test was later modified by AVCO and adopted as the standard test. Modifications comprised increasing the opening of the flask to 3 1/2 inches and using a 60 instead of a 14 mesh screen; second degree of severity conditions only are used.
- c. Cyanamids' test methods for synthetic fluid cracking catalyst.
- d. Albany Metallurgy Research Center - the air-lift and fluid-bed equipment and test procedure.
- e. Standard Oil Company (Indiana) test method of Forsythe and Hertwig.

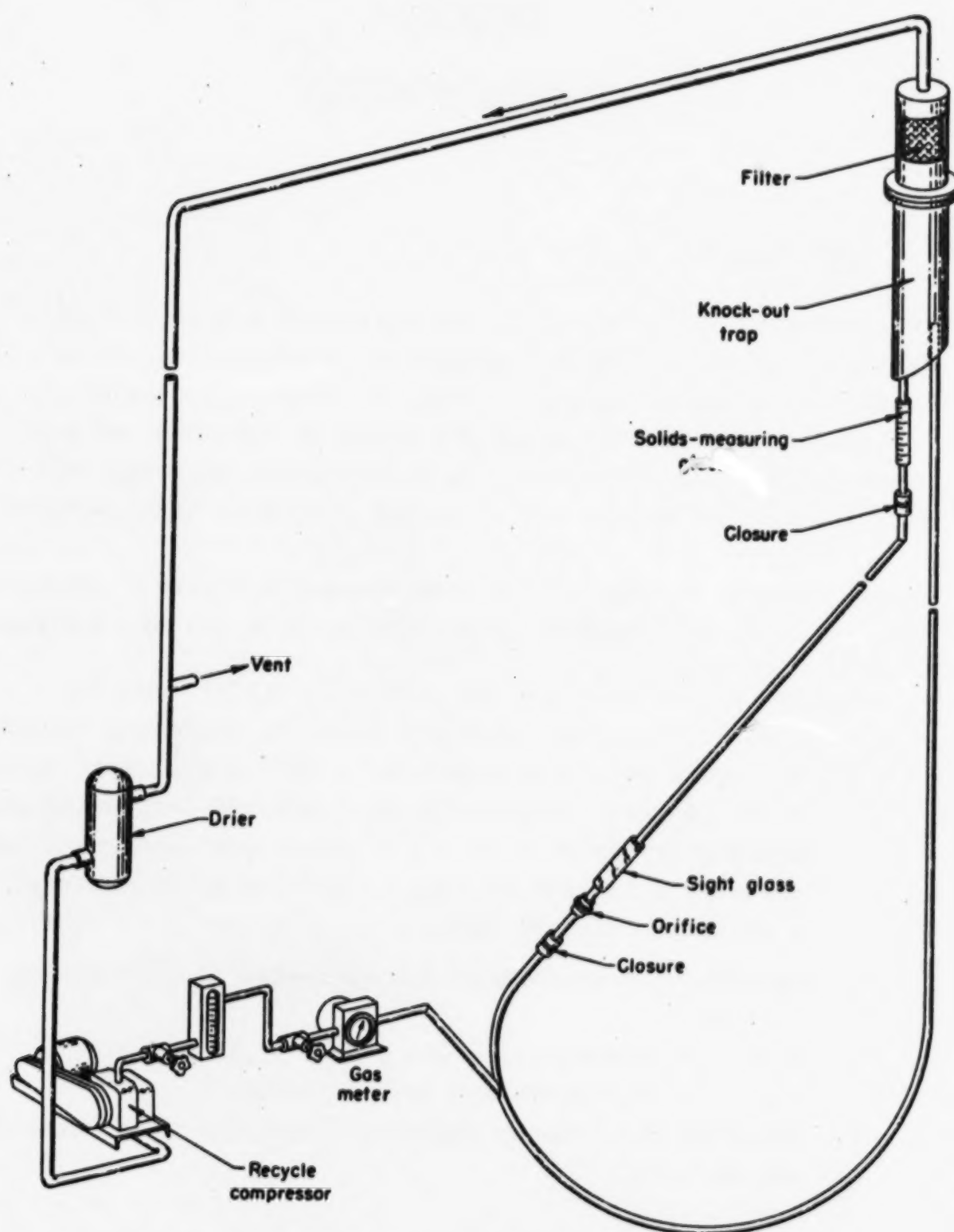


FIGURE A-59 - Pneumatic Conveying of Alkalinized Alumina.

1/22/60

ACCELERATED
AIR - JET ATTRITION TEST
FOR ALKALIZED ALUMINA
W. R. GRACE & CO.

A. T. Lengade
Tech. Service Lab., Curtis Bay
December 5, 1967

Accelerated Air Jet Attrition (A.A.J.A.)

Because of the need for outstanding attrition characteristics of a sorbent, a new attrition test was developed for testing alkalized alumina beads. A lot of significance in this test has been placed by Oil Industry which they find correlates rather well with attriting tendency of catalyst in their pneumatic lift units.

The attached figure (page 2) illustrates the Air Jet apparatus.

Description of the apparatus:

- 1: Compressed air inlet with pressure = 27 psig
temperature = 65°F. to 75°F.
dew point = -35°F. to -45°F.
- 2: 1/4" needle valve
- 3: 1/4" steel nipple
- 4: 1/4" x 1/2" steel bushing
- 5: 1/2" solenoid valve - skinner electric valve Div. Conn.,
115 volts, 60w, 8 watts, 150 psi. Valve #LC2DB4150, normally closed.
- 6: Universal timer - Dimco Gray Co.
- 7: 1/2" steel nipple
- 8: 1/2" x 3/4" steel bushing
- 9: Flowmeter - Fischer & Porter Co. #6111 A329 3B1. Precision
bore florator tube #FP-3/4-27-G-10
- 10: 3/4" x 1/2" steel bushing
- 11: 1/2" iron nipple length = 1"
- 12: 1/2" Globe valve
- 13: 1/2" x 3/8" steel bushing
- 14: Imperial brass hose connector - connecting 3/8" bushing with
1/2" plastic tubing.
- 15: 1/2" I.D. flexible plastic tubing length = 40"
- 16: 1/4" steel pipe length = 2"
- 17: 0 to 30# pressure gauge
- 18: 1/4" steel tee
- 19: 1/4" x 1/4" half union coupling, Imperial
- 20: 1/4" copper tubing
- 21: 1/4" nut, Imperial

- 22: 1/4" x 1/4" half union coupling, Imperial
- 23: 1/4" x 1/4" steel coupling
- 24: 1/4" x 1/4" hose connection, Imperial Brass
- 25: Rubber stopper No. 9 Neoprene, concave surface 7/16" deep
- 26: 1000 ml conical flask with 1" hole in bottom, Pyrex No. 4984
- 27: No. 14 mesh support screens (upper - 2 1/2" x 2 1/2", lower 1 3/4" x 1 3/4") bolted into position.

Working Principle:

Dry air is admitted for a certain period of time, through a concave stopper at a certain flow rate. The attrition of the preweighed sample is done by air. At the end of test, the material is rescreened on #14 mesh and the retained material is weighed. Attrition values are reported as the weight percent loss.

Established conditions for testing Alkalized Alumina beads with the following properties:

Shape	Spherical
Size	8 to 14 mesh
Average Bulk Density	40 to 50 lbs./cu.ft.
Total Volatile at 300°F.	2.0%

Testing Conditions:

<u>Degree of Severity</u>	<u>Ist</u>	<u>IIInd</u>	<u>IIIrd</u>
Rotameter Reading, %	26	30	35
Volumetric Flow Rate in S.C.F.M.	3.0	3.55	4.25
Time in hours	2.5	1	.5
Screen Mesh	14	14	14

All attrition losses for I, II, and III degree are reported on an average time of 1/2 hour.

Standard Procedure for IIIrd Degree Severity for Alkalized Alumina Beads:

A 30 gram sorbent sample (+ 0.1 gram) previously screened on a No. 14 U.S. Standard Screen is placed in an inverted one liter conical flask (26). The flask has a one-inch hole centered in its bottom which

is covered by a 14 mesh screen. Dry air (-40°F. D.P.) is admitted for 1/2 hour through a concave stopper at 4.25 S.C.F.M. flow rate. At the end of 1/2 hour, the material is rescreened on a U.S. #14 mesh screen and the retained material is weighed (X grams). Attrition values are reported as follows:

Let X=grams material have been retained on #14 mesh after attrition.

$$\text{Then } \frac{30 - (30 - X)}{30} \times 100 = \% \text{ attrition loss}$$

Same procedure is followed for Ist and IInd Degree Severity except for time which is 2 1/2 hours for Ist degree and 1 hour for IInd degree. But the attrition loss is reported on an average time of 1/2 hour. Results in a given piece of apparatus have generally been reproducible within a maximum deviation of $\pm 10\%$ of test results.

A typical result of % attrition loss of alkalized alumina has been reported in Table #1.

TABLE A-56

<u>Alkalized Alumina</u>	<u>% Attrition Loss</u>
Ist Degree of Severity	8
IInd Degree of Severity	11
IIInd Degree of Severity	15

NOT REPRODUCIBLE

Needed Correlation between test results & plant performance.

ERRATA

30 - X = Weight Loss

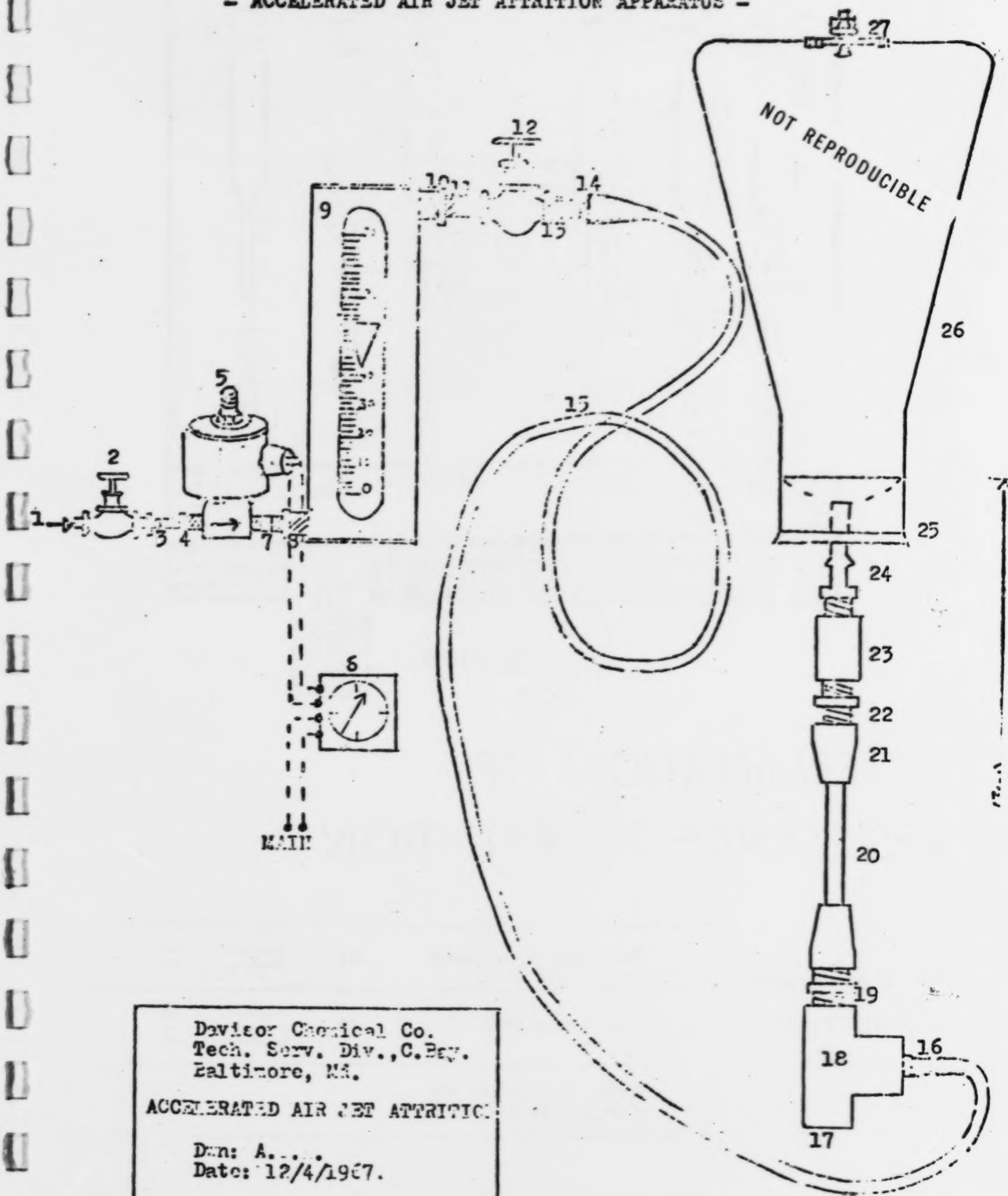
then $\left[\frac{30 - (30 - X)}{30} \right] 100 = 100 - \% \text{ Attrition Loss}$

$\left[\frac{(30 - X)}{30} \right] 100 = \% \text{ Attrition Loss}$

FIGURE A-60

- ACCELERATED AIR JET ATTRITION APPARATUS -

2

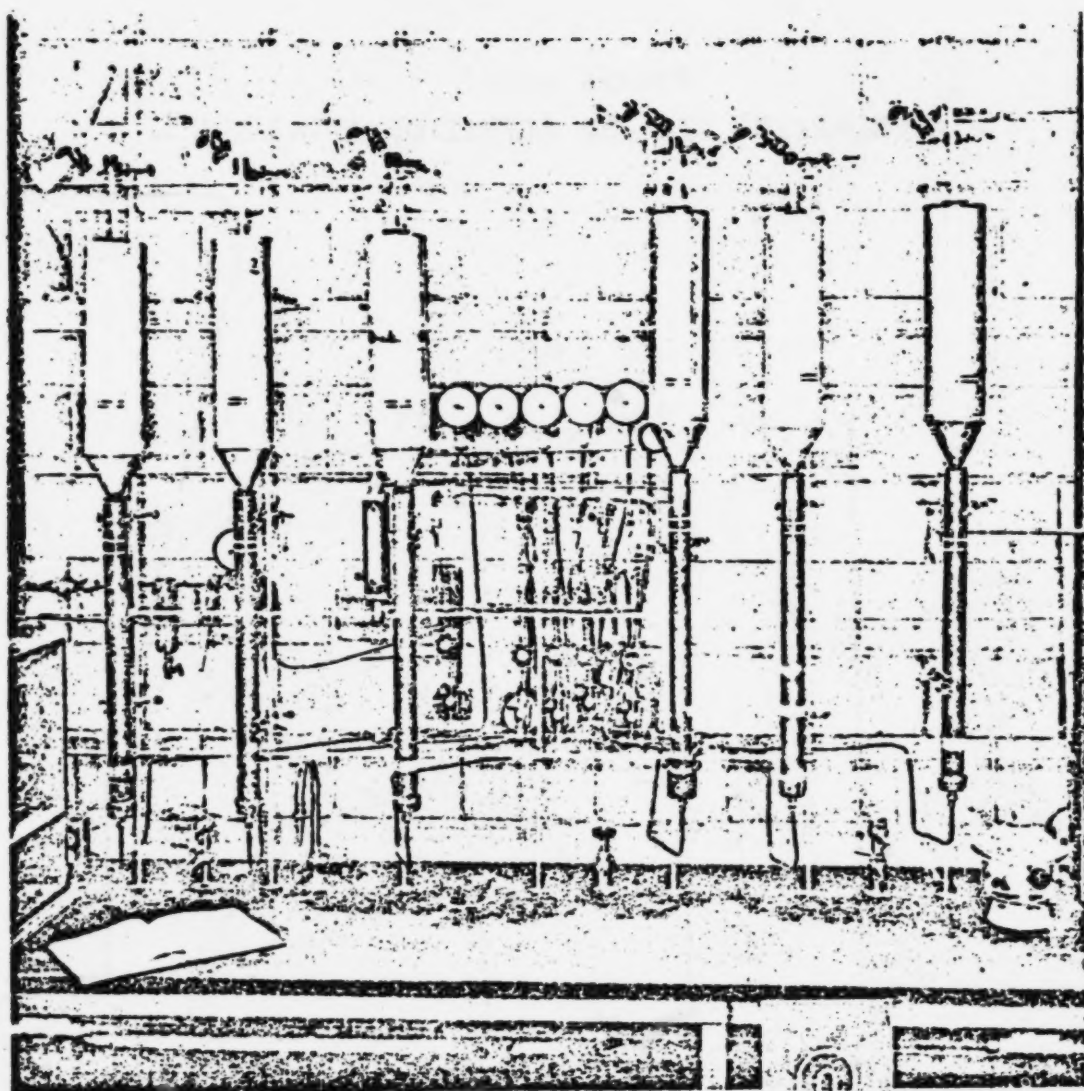


Davison Chemical Co.
Tech. Serv. Div., C. Bay.
Baltimore, Md.

ACCELERATED AIR JET ATTRITION

Des: A.....
Date: 12/4/1967.

NOT REPRODUCIBLE



SECTION



DETERMINATION OF RESISTANCE TO ATTRITION

CYANAMID TEST METHODS
FOR SYNTHETIC FLUID
CRACKING CATALYST

FORTY-FIVE HOUR METHOD	43	Apparatus	43
		Procedure	44
ONE-HOUR METHOD	46	Apparatus	46
		Procedure	46
		Calculations	48
EFFECT OF ATTRITION ON PARTICLE SIZE DISTRIBUTION	49		

Fine catalyst dust capable of escaping from the recovery equipment of commercial fluid cracking units is produced in part by the attrition of catalyst particles as they collide with each other and with the walls of the equipment. This attrition is accelerated when such collisions occur at high velocities.

Laboratory tests to measure the resistance to attrition of fresh or equilibrium catalyst are conducted under conditions approximating those in the commercial fluid cracking process. At the present time, experience and observations have not revealed any clear-cut, simple, quantitative relationship between laboratory and commercial results. It is important, nevertheless, to continue such laboratory studies as a guide for the development of new catalysts and as a means of advancing the technology of fluid catalytic cracking.

Two tests, the Forty-five Hour and the One-hour, are employed by the Cyanamid laboratories. In both, air jets impart high velocities to some of the particles in a bed of catalyst. The collision of these particles with others in the system produces attrition.

Of the two tests, the Forty-five Hour method is believed to give a closer approximation of the conditions that exist in commercial cracking units. The One-hour method is a quick, approximate measure of attrition, useful for comparison of catalyst samples.

FORTY-FIVE HOUR METHOD

The Forty-five Hour method measures attrition at an air jet velocity of 890 ft./sec. Fine catalyst is removed continually from the attrition zone by elutriation into a flask-thimble assembly, which is weighed at intervals. These test conditions are similar to those usually encountered in refinery operations. The attrited or overhead catalyst so measured is expressed as the weight per cent overhead, and is a rough estimate of the particles that would pass out the stack of a commercial cracking unit.

APPARATUS

Source for compressed air
Pressure regulator
Rotameter, range 2-20 SCF/H air at operating pressure
Moore Flow Controller, Type 63BU
Pressure gauge, 0-50 lbs.
Perforated plate (See Figure 20). Tungsten carbide

draw plate inserts with 0.0150 ± 0.0002 " holes from W. Dixon Company, Newark, N. J. may be inserted in larger holes in the plate instead of drilling the small holes.

Brass tubing, $27\frac{1}{2}$ " x $1\frac{1}{2}$ ", I.D.

Stainless steel sheet, 22" x 5", thin walled, for upper section of apparatus

Glass tubing, $9/16$ " Diam.

Filter flask, 250-ml.

Extraction thimbles; 43 mm. diam. x 123 mm. long (Greens #733 from Fisher Scientific Company)

Ball joint clamp for holding flask assembly in place (1 part from #35 and 1 part from #28)

Hose clamp, $1\frac{1}{2}$ " O.D., to hold thimble in place

Rubber stoppers, two #9, one #10, and one #4

Needle valve, Hoke, one #341 (1" taper)

Needle valves, Hoke, ordinary (or preferably #450 Hoke toggle valves)

Copper tubing, $\frac{1}{4}$ ", and suitable pipe and flare fittings

Harvard Trip Balance

The apparatus is shown in Figure 20, p. 44.¹ It is designed to admit air through the opening of a perforated plate at sufficient velocity to cause jets of catalyst to be blown into the main bed of the catalyst at fairly high velocity.

The large upper section above the catalyst tube serves as an elutriator-dust collector. As such, the particles with diameters over approximately 16 microns (depending somewhat on density of the particles and Stokes Law²) fall back and concentrate on the outer walls of the 5" diameter tube. There they become agglomerated into large enough aggregates to drop back into the catalyst bed.

Particles with diameters smaller than 16 microns² are carried over into a flask-thimble assembly that can be weighed at intervals to determine the amount of fines formed as a function of time. Of course, different flow rates and/or upper sections of different diameter than the 5" tube will cause other diameter catalyst to pass overhead.

Assemble the apparatus as shown in Figure 20, p. 44. The 0.0150" holes in the perforated plate should be drilled to close tolerances, because the attrition depends markedly on diameter of the holes. Some erosion of the holes occurs during use, and the disc must be replaced after several months of continuous use. For this reason, it is advisable to run a standard sample weekly and to note the pres-

¹ The apparatus is a modification of that used by Forsthe and Hertwig, *Ind. Eng. Chem.* 41, 1200 (1949).

² See page 34.

• Apparatus for Determination of Attrition

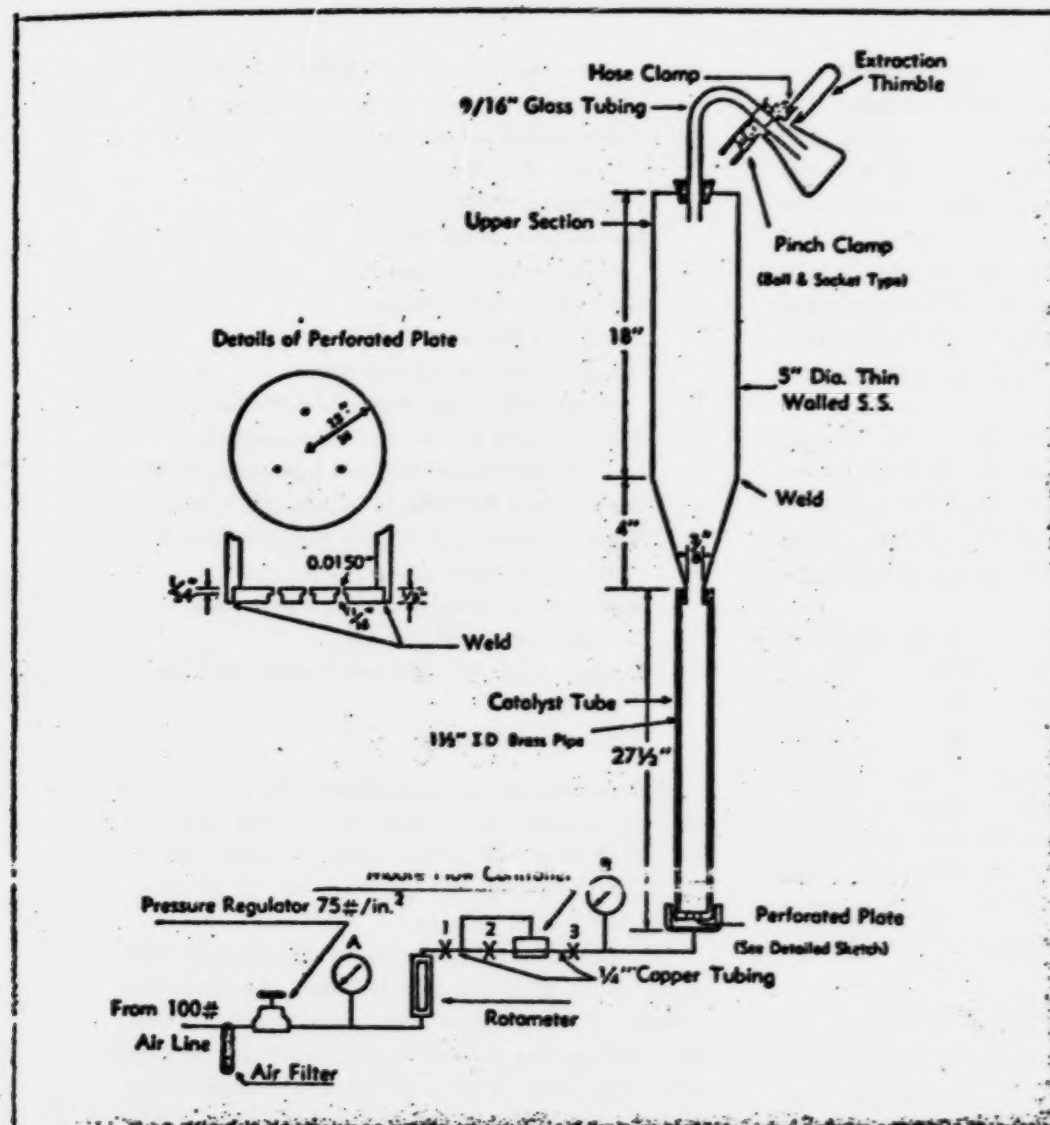


FIGURE A-61

sure drop through the plate (Gauge B). This drop usually decreases when the holes become worn sufficiently to affect the results.

PROCEDURE

Weigh the flask and thimble assembly.

Connect the attrition section to the air line, crack valve (1).

Add 5 g. of water to 45 g. of dried and calcined cracking catalyst and weigh. Charge the catalyst tube with this material.

Put the stainless steel tube and weighed flask and thimble assembly in place.

Set the air pressure through calibrated rotameter at 75 p.s.i.g.

Open valves (1 and 3) and by means of valve (2) adjust the air flow to 15.00 ± 0.1 CF/H at room conditions

Remove and weigh flask and thimble assembly at intervals such as 5, 20, and 45 hours and plot the % overhead versus time as shown in Figure 21, p. 45. The overhead is comprised of both initial fines and fines due to attrition. Calculate the per cent attrition at 5, 20 and 45 hours on a wet, fines-free basis as follows:

$$\% \text{ Attrition} = 100 \times \frac{\% \text{ Overhead} - \% \text{ Initial "Fines"}}{100 - \% \text{ Initial "Fines"}}$$

The initial amount of "fines" may be determined by subsieve analyses and knowledge of the particle size maximum in the overhead. (Section V, p. 24). Or it may be estimated from the intercept of the 5-hour tangent of the overhead versus time curve shown in Figure 22, p. 46. The time required to eliminate 95% of the initial fines probably ranges from 2-8 hours, depending on the amount present originally. The elutriation process can be speeded by tapping or vibrating the upper section.

The compressor at the Stamford laboratories of American Cyanamid Company compresses the air to 100 p.s.i.g., so that the air invariably is saturated after being compressed under prevailing atmospheric conditions. When it reaches the catalyst, therefore, it has a relative humidity of 15/115. No attempt is made to dry the air as electrostatic effects are reduced when some moisture is present. The small gain or loss in weight due to change of moisture content of the sample can be neglected.

If 10% water content for overhead catalyst (normal value for fresh catalyst) and a skeletal density of 2.50 g./cc. are assumed and Stokes Law is applied, the particle size maximum of the "fines" depends on pore volume as follows:

PV	Particle Size (Microns)
0.2	13.3
0.4	15.3
0.6	17.1
0.8	18.7
1.0	20.3

A sample calculation is given below and results are plotted in Figure 23, p. 46.

Pore Volume = 0.96

Particle size maximum of fines = 20 microns

Weight per cent of initial fines (-20μ) = 7.0

$$\text{Per cent attrition at 5 hrs.} = \frac{(12.2 - 7)}{(100 - 7)} 100 = 6.2$$

$$\text{Per cent attrition at 20 hrs.} = \frac{(19 - 7)}{(100 - 7)} 100 = 12.9$$

$$\text{Per cent attrition at 45 hrs.} = \frac{(23.5 - 7)}{(100 - 7)} 100 = 17.7$$

TABLE A-57

Attrition Resistance Data Sheet

FORTY-FIVE HOUR METHOD								
Attrition Run. No. _____				Unit No. _____				
Sample _____								
Heat Treatment _____		1	Hrs.	Temperature _____		1100	°F.	Sample weight _____ 50 g.
Date	Sampling Time	Elapsed Hours	P	Rotameter Reading	Total Weight, g.	Weight Over, g.	Weight Over, %	Attrition %
9/14	10:15	—	14.7	13.7	57.42	—	—	—
9/14	3:15	5¼	14.5	13.7	63.56	6.1	12.2	6.2
9/15	9:00	22¾	14.9	13.8	67.15	9.7	19.4	12.9
9/16	9:15	47	14.4	13.7	68.25	11.9	23.8	17.7

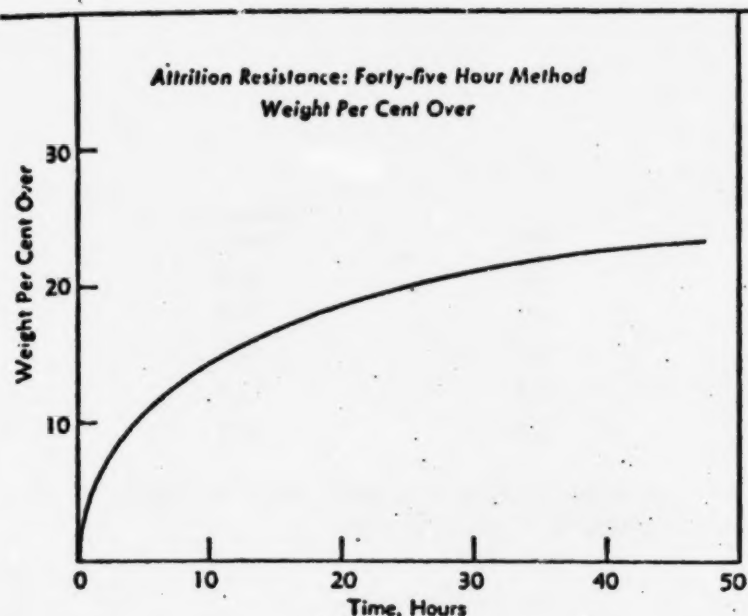


FIGURE A-62

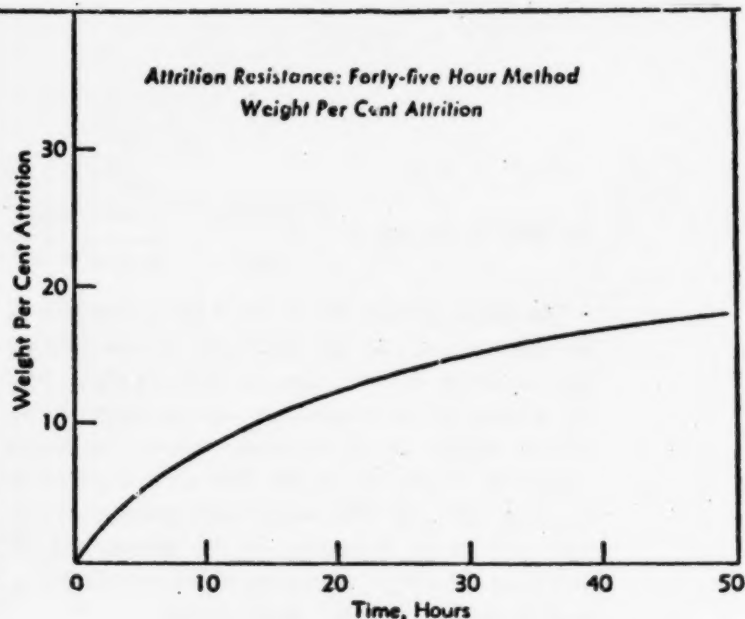


FIGURE A-63

ONE-HOUR ATTRITION METHOD¹

The One-hour method evaluates attrition on the basis of the change in the minus 20-micron content of the sample by treatment with an air jet at a linear velocity of 2670 ft./sec. The attrition in one hour is approximately equal to that obtained by the Forty-five hour method.

The fines produced are not separated from, but returned to, the main catalyst bed. What specific effect these fines have on the attrition mechanism has not been determined as yet.

APPARATUS (See Figure 24, p. 47)

- 250-ml. graduated cylinder
- 4-oz. stoppered bottle
- Glass funnel
- Tared, stoppered, 8-oz. bottle
- Source for compressed air
- Pressure regulator
- Rotameter, range 2-20 SCF/H air at operating pressure
- Moore Flow Controller, Type 63 BU
- Pressure gauge (2) 0-100 lbs.
- Perforated plate
- Flanged PYREX glass pipe, 1" I.D. x 5.0'
- Extraction thimbles, 40 mm. diam. x 123 mm. long (Greens #733)

- Gooch tubing, 1 1/2" diam. to hold thimble on glass pipe
- Needle valve, Hoke #341, 1" taper
- Toggle valves, Hoke #450
- Copper tubing, 1/4" with suitable fittings
- Harvard Trip Balance

Assemble the apparatus as shown in Figure 24, p. 47. The 0.0150" hole in the plate should be drilled to close tolerance, because the attrition depends markedly on the diameter of the hole. Some erosion of the hole occurs during use. A standard sample should be run weekly, noting the pressure drop across the plate. When the hole becomes worn enough to affect the results, replace the perforated plate.

PROCEDURE

Weigh a 250-cc. graduated cylinder.

Fill the graduate with catalyst up to the 80-cc. level. Tap the graduate on a firm surface until a constant, compacted level is obtained. Continue adding catalyst and tapping until the compacted level reaches 80 cc. Weigh the filled graduate and determine the weight of the catalyst sample.

Transfer the sample to a 4-oz. bottle. Add water in an amount equal to 10% of its weight. Break up the lumps with a spatula. Stopper the bottle and shake it to disperse the water evenly.²

¹ This method is basically the same as that developed by Standard Oil Company (Indiana). Published *Ind. Eng. Chem.* 41, 1200 (1949).

² Humidification minimizes build-up of static charge and avoids accumulation of charged particles on the apparatus during the test.

Clamp the attrition column securely in a vertical position and connect the air inlet.

Pour the humidified sample from the bottle onto a clean piece of hard-surfaced paper. Use a brush to remove all adhering particles from the bottle. Insert a funnel into the glass column and pour the catalyst from the paper into the column being careful to avoid spilling.

Weigh the thimble and fit it onto the top of the column and secure tightly by means of Gooch rubber tubing.

Set the air pressure through the calibrated rotameter at 70 p.s.i.g. (gauge A, Figure 24).

Open valves (1 and 3), and adjust the air flow by means of the control needle, valve (2), to give a rotameter setting equivalent to an air rate of 16.3 CF/H at room conditions.

Record the exact time of starting the air flow.

Maintain the air pressure at 70 ± 0.5 p.s.i.g. throughout the run.

The particles in the bed should be moving downward along the glass walls at the bottom of the pipe

so that the bed will be mixed. The length of the 0.0150" hole should be such that pressure drop across the plate (gauge B) is in the range of 55-60 p.s.i.g. (ca., 1/24").

After exactly 60 minutes, shut off the air.

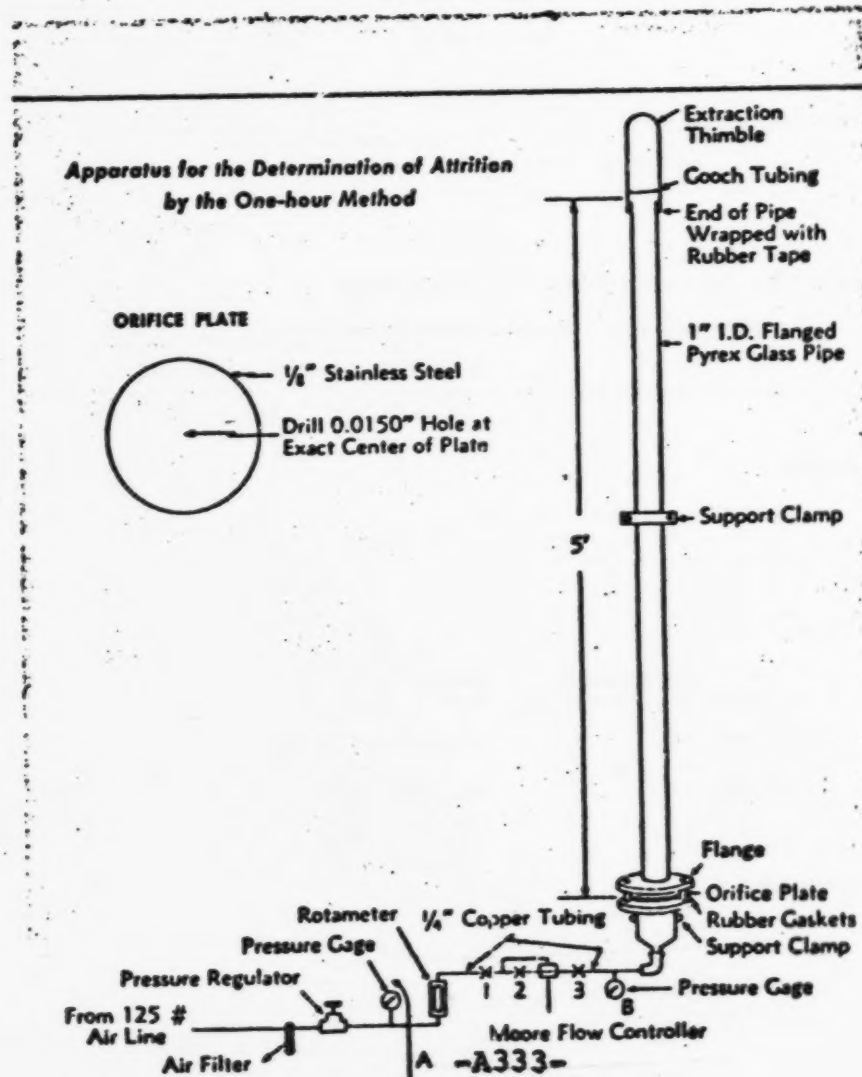
Tap the thimble vigorously to return the catalyst fines to the main part of the sample. Remove the thimble from the column and weigh.

Unclamp the column and carefully pour the catalyst onto a clean piece of hard-surfaced paper. If a significant amount of particles cannot be dislodged from the column, wash it with acetone. Dry the recovered fines and add them to attrited catalyst samples. Transfer the total recovered catalyst into a tared, stoppered, 8-oz. bottle. Weigh the total recovered catalyst.

Prepare the sample for determination of the minus 20-micron content by subsieve analysis (See Section V, p. 26).¹

¹ If sedimentation is used as the subsieve method of analysis, the attrited sample slurry should be mixed in a Waring blender to break up the agglomerations of fine particles.

FIGURE A-64



CALCULATIONS

Per cent nonrecoverable fines. The increase in weight of the thimble is assumed to represent 0 to 10 micron particles, which are too fine to be dislodged by tapping. These particles must be included in the

subsieve analysis after attrition and may be determined by means of the following expression:

$$F = \frac{100 \times N}{T}$$

TABLE A-58

• Sample Worksheet used in the Determination of Attrition by the One-Hour Method

Lab. No. _____		Date _____	
Car No. _____		Grade _____	
Weight of thimble, g.		Weight of sample, g.	
Final	6.4	Final	47.0
Initial	6.0	Initial	45.6
Increase (N)	0.4		
		Pressure, p.s.i.g.	
		A	70
		B	56
		Pore volume, cc./g.	
		0.80	
		Minus 20-micron fraction, initial weight %	
		5.1	
		Rotameter reading	
		16.3	
		Air rate, L./min	
		10.0	

Per Cent Nonrecoverable Fines

$$F = \frac{100 \times N}{T} = \frac{100 \times 0.4}{47.0} = 0.85$$

Correction of Minus 20-Micron Analysis for Thimble Fines

Weight per cent of —20-micron fraction as run,¹ a = 16.3

$$\text{Corrected per cent finer} = \frac{(a + F) 100}{100 + F} = \frac{(16.3 + 0.85) 100}{100 + 0.85} = 17.0$$

Rate of Attrition

$$\frac{A \times 100}{B} = \frac{(17.0 - 5.1) 100}{100 - 5.1} = 12.6$$

Test Recovery

LOI on initial sample, % 14.2
LOI in recovered sample, % 20.3

$$\frac{T (100 - V_i)}{S (100 - V_j)} \times 100 = \frac{47.0 (100 - 14.2) 100}{45.6 (100 - 20.3)} = 97.8\%$$

¹ Sedimentation result.

where F = Nonrecoverable fines, %
 N = Increase in weight of thimble, g.
 T = Total weight of catalyst recovered
 from attrition test, g.

Correction of Minus 20-Micron Analysis for Thimble Fines

$$\begin{aligned} \text{Particle size} &= 20 \text{ microns} \\ \text{Per cent finer as run} &= a \\ \text{Corrected per cent finer} &= \frac{(a + F) 100}{100 + F} \end{aligned}$$

Rate of Attrition. Relative rates of attrition for catalysts are calculated as the increase in fines content caused by the standardized treatment for attrition. The rate of attrition is based on the difference in the quantity of 0 — 20-micron fraction present, as shown by micron analysis before and after attrition, and is determined by the following expression:

$$\text{Attrition rate} = \frac{A \times 100}{B}$$

where

A = Increase in weight per cent of
0 — 20-micron fraction present
 B = Weight per cent of plus 20-micron
material in charge

Test Recovery

$$\% \text{ Recovery} = \frac{T (100 - V_r)}{S (100 - V_o)} \times 100$$

where

T = Total weight of recovered
catalyst, g.
 S = Weight of original sample before
humidification, g.
 V_r = Volatile content of recovered
catalyst, %
 V_o = Volatile content of original
sample, %

EFFECT OF ATTRITION ON PARTICLE SIZE DISTRIBUTION

Attrition effects appreciable change in the particle size distribution of fluid cracking catalyst. The degree to which this change occurs can be measured by determining the particle size distribution of the catalyst before and after attrition.

In the following example, particle size distribution was determined by sieve sedimentation (see Section V, p. 24), and attrition by the One-hour method. However, sieve-CAE Roller and/or the Forty-five Hour attrition method can be used.

Particle Size Distribution

TABLE A-59

Particle Size (Microns)	Per Cent Finer (Before Attrition)	Per Cent Finer (After Attrition)
150	100	100
100	92	95
80	80	87
74	74	83
60	56	71
50	41	61
40	26	46
30	13	31
20	5	17
10	1	6

ALBANY METALLURGY RESEARCH CENTER

ATTRITION TEST METHODS

Fluidized-Bed Attritioning Equipment

The fluidized-bed attritioner consists of a "Roots" low pressure blower ($60\text{ft}^3/\text{min}$), a 2-inch manifold with 1/4-inch outlets to each fluidized bed, a laboratory-built electric furnace (hot-zone 12" x 12" x 60") and 12 "Vicor" fluidizing tubes. The fluidizing tubes are 2 inches in diameter and 16 inches long, with a 3-inch diameter by 6-inch bell on the upper end to reduce air velocity and thus retain attritioned material. The feed ends of the fluidizing tubes are tapered at about 60° , from 2 inches down to just under 3/8 inch, to retain 3/8-inch steel balls used to disperse the air as it enters the bed. The air is not preheated before entering the fluidized beds; therefore, there is a temperature gradient across the bed of from room temperature to 300°C .

Attritioning-Testing Procedure

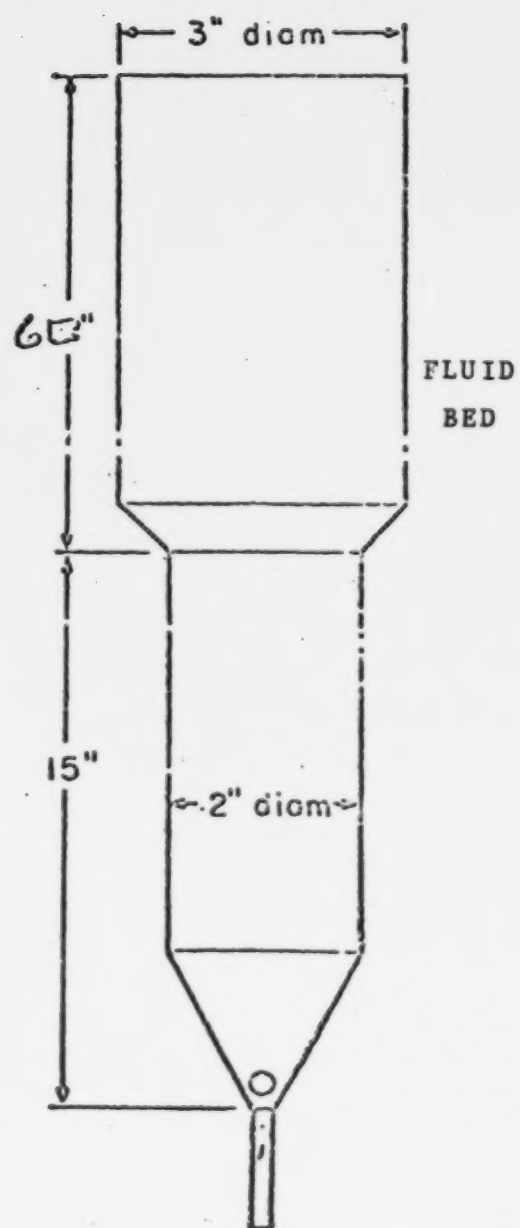
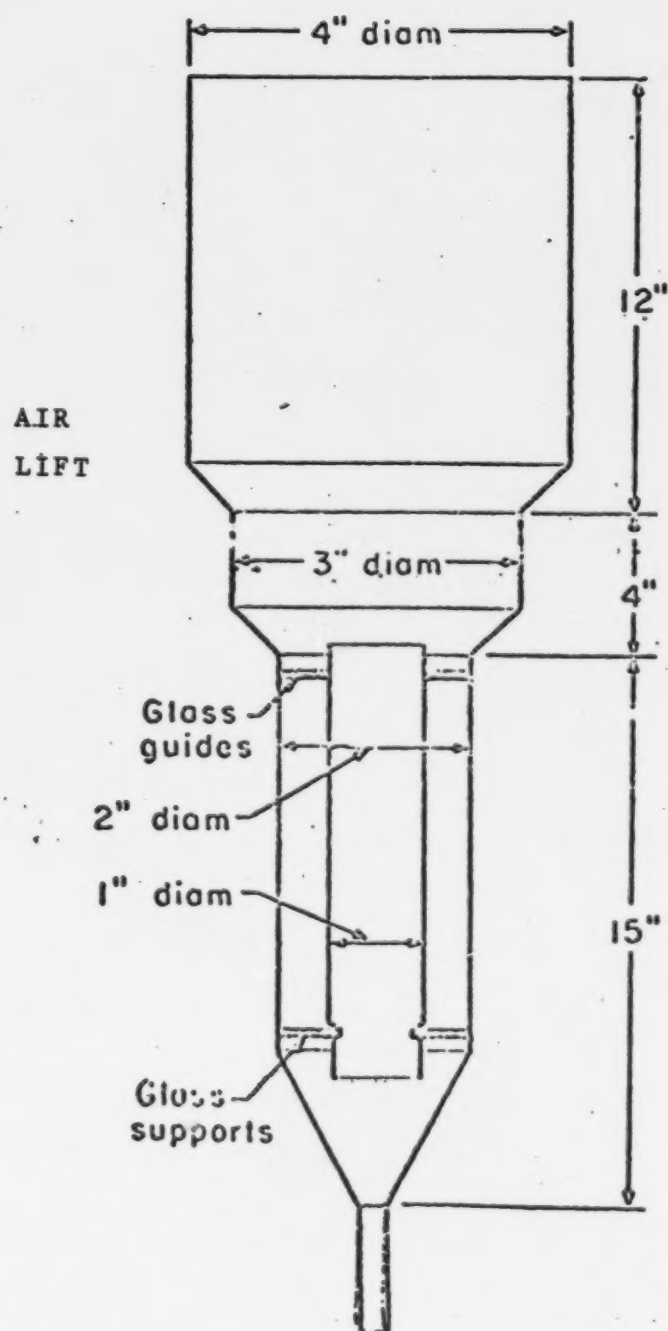
1. Representative 50-gram samples of each product to be treated are weighed and sized to obtain the size distribution of the material.
2. Samples are then charged into the top of the fluidizing tubes and the air adjusted to produce a turbulent bed. Gas velocity through the bed is about 1.8 ft/sec.
3. Every 24 hours the charge is weighed and additional material is added to maintain a 50-gram charge.

4. The 50-gram charge was screened to determine the change in size distribution of the material after completion of the 15-day attritioning test period.

5. Air-lift attritioning sample size was 10 grams and the gas velocity about 25 ft/sec.

6. 80 mesh screen on top.

FIGURE A-65



Attrition Characteristics of Fluid Cracking Catalysts • Laboratory Studies

Catalyst attrition, or particle breakdown, in a fluid-catalytic cracking unit is an important factor in operating costs, as it directly affects the losses of catalyst from a unit. A simplified laboratory accelerated-attrition test has provided useful data for evaluating attrition resistance. The catalyst is subjected to the action of a high-velocity air jet; the extent of particle breakdown is determined by screen and Roller analyses. A comparison of test data on commercial grades of fresh natural, silica-alumina, and silica-magnesia ground catalysts shows that all are within the same range of attrition resistance. Fresh microspheroidal catalysts show better resistance to breakdown than ground catalysts except where there are excessive proportions of agglomerates. The effect on attrition

resistance of heat pretreatment at 1100° F. varies with different catalysts. Silica-magnesia catalyst showed the greatest increase in attrition resistance among the ground catalysts, while microspheroidal silica-alumina samples showed little change. Attrition data on catalyst samples from the start of runs in a commercial fluid-cracking unit with fresh synthetic ground catalysts show that the attrition resistance is greatly improved during a short period of operation. A comparison of commercial and pilot plant data indicates that the greater part of this increase in attrition resistance results from mechanical action on the particles. The smaller effect of subjection to cracking operations is similar to the laboratory observation on heat-treated catalysts.

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FLUID catalytic cracking (3) has become one of the principal processes in petroleum refining. The most important feature of this process is the maintenance in a fluidized condition of a powdered catalyst which ranges in particle size from less than 1 to over 100 microns. Appreciable quantities of this relatively expensive catalyst are lost from a fluid-cracking unit because of the incomplete recovery of fine catalyst particles from the regenerator flue gases by cyclones and Cottrell precipitators. Furthermore, in some recently designed cracking units Cottrell precipitators have been omitted, and all the particles finer than about 20 microns are rapidly lost through the cyclone separators. In addition to the 0-to-20-micron particles present in the fresh catalyst charged to the unit, fines in this size range are produced during operation by the attrition of the coarser particles. Consequently, to minimize losses of catalyst fines, the catalyst must have good resistance to attrition.

Information on attrition resistance is therefore an important factor in the laboratory evaluation of a new cracking catalyst, which involves a comparison with the attrition resistance of a commercially acceptable catalyst. In order to provide data for these comparisons, a laboratory accelerated-attrition test was developed to determine the relative resistance to particle breakdown of various catalysts. This paper describes the test, evaluates some of the factors influencing catalyst attrition, and presents attrition data on a number of different cracking catalysts.

Attrition of catalyst in a commercial fluid-cracking unit is caused by several factors, including collisions between catalyst particles and impact and abrasion of the particles upon the walls of vessels and catalyst carrier lines. In the design of a suitable laboratory test for comparing the attrition resistance of various catalysts, it was desirable to reproduce as nearly as possible the above mechanism of particle breakdown, so that the results would be representative of commercial operation. Although it was not possible to reproduce exactly the plant conditions on a laboratory scale, it developed that a high-velocity air jet impinging on a bed of catalyst particles was a readily controlled means for attrition of catalyst and gave the desired accelerated breakdown rate.

In the present test, the charge of catalyst is subjected to the action of a single air jet for a fixed period of time. The break-

down shown by the change in particle-size distribution is compared with that for other catalysts under the same conditions. Although the comparisons of catalysts are relative and do not permit direct quantitative predictions of actual plant losses, the test results have been useful in laboratory evaluation of new catalysts for commercial operations. In addition, information has been obtained on the trend of catalyst attrition resistance with length of time of operation in a commercial unit.

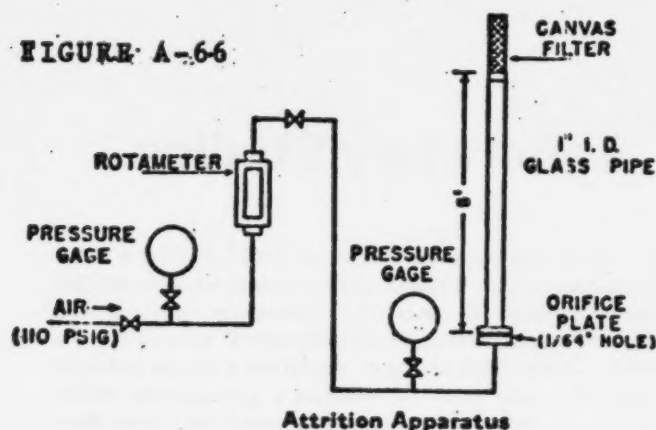
In contrast with the conditions in a commercial unit, the fines produced by attrition are retained in the test apparatus, so that the severity of attrition on the remaining coarse particles is somewhat reduced. As a second deviation from plant operation, the attrition in the test is presumably caused by the collisions of particles rapidly accelerated by the air jet with slower moving particles; hence there is no effect of particles hitting pipe walls or obstructions. The advantages inherent in this test method—small catalyst charge, simplified apparatus and operating procedure, good reproducibility, and short time requirement—are believed to offset the advantages of possibly closer approaches to plant attrition conditions that could be obtained with a more complicated method.

From the standpoint of attrition resistance, the catalysts commercially available for use in fluid-cracking operations may be divided into two principal types: ground catalysts and microspheroidal (MS) catalysts. Fresh-ground catalysts have generally irregular shapes with sharp edges and protruding corners. Microspheroidal catalysts, as the name indicates, have spherical shapes and smooth surfaces. The spherical shape was sought in order to reduce attrition losses from cracking units by eliminating the catalyst surface irregularities which give rise to high initial breakdown rates.

ATTRITION APPARATUS

A diagram of the attrition apparatus is presented in Figure 1. The catalyst at room temperature is subjected to the attrition action of a high-velocity air jet issuing from a $\frac{1}{4}$ -inch orifice at the center of a $\frac{1}{4}$ -inch stainless-steel plate. This orifice plate is bolted between flanges at the bottom of a vertical 5-foot section of 1-inch-inside-diameter Pyrex pipe. The high-pressure air supply is reduced to 70 pounds per square inch gage by means of the

FIGURE A-66



pressure-reducing valve. The air rate is measured with a rotameter and controlled by a needle valve downstream of the rotameter. A pressure gage upstream of the orifice plate indicates the pressure drop across the orifice. A canvas filter bag is clamped securely at the top of the glass pipe in order to prevent loss of catalyst entrained in the exit air stream.

TEST PROCEDURE

In this laboratory accelerated-attribution test a weighed catalyst sample is subjected to the jet attrition action for 1 hour. The resulting change in distribution of catalyst particle size is determined by screen and Roller analyses. The more pertinent details of the attrition procedure and particle-size analyses are described below.

Attrition Procedure. A representative 50-gram sample of the catalyst is charged into the top of the glass pipe, and the weighed sample is subjected to the jet attrition action for 1 hour. This air rate corresponds to a superficial velocity of about 0.8 foot per second in the glass pipe, which thoroughly fluidizes the catalyst bed and provides good mixing of the particles. The pressure upstream of the orifice plate is 55 to 58 pounds per square inch gage under these conditions, and the air velocity in the jet approaches the speed of sound. Catalyst particles in its path are very rapidly accelerated and collide with the slower moving particles in the aerated bed. These high-speed collisions cause the attrition of the catalyst particles in this test.

During the test, the glass pipe and filter bag are periodically tapped in order to return to the bed any catalyst that has stuck to the wall or canvas filter. Following the test period, the catalyst is recovered as completely as possible from the pipe and the filter. Acetone is used to wash free any catalyst particles that have stuck to the pipe walls. The canvas bag is weighed to determine the quantity of catalyst fines not directly recoverable. These fines are included in the particle-size analyses in the finest size fraction. Including the fines in the bag, the catalyst recovery is seldom less than 97% of the charge. To correct the weight of recovered catalyst for any change in moisture content during the test, volatile content at 2200° F. is determined on the catalyst before and after attrition.

Screen Analyses. The screen-analysis data presented in this paper are based on the Tyler standard series from 80 through 325 mesh using a combination wet- and dry-screening method. A representative 25.0-gram sample of catalyst is placed on a 325-mesh screen, and the finest particles are washed through with water. The catalyst remaining on the screen is then washed with acetone to remove excess water and dried for 1 hour in an oven at 220° F.

This wet method eliminates the passage of large amounts of fine particles through the whole series of screens and thus greatly minimizes possible inaccuracies due to agglomeration of fines (1) or electrostatic effects (7).

After being cooled and weighed, the catalyst is dry-screened in a Tyler Ro-Tap shaker on the above screen series. Shaking periods of 30 minutes are repeated until no fraction changes in weight by more than 0.2 gram; three or four such periods are usually sufficient. The percentages of the individual fractions coarser than 325-mesh are calculated from the final weighing, and the -325-mesh fraction is obtained by difference, as the fines from the wet-screening are not recovered. The small loss occurring during the dry-screening is proportioned among all the fractions.

The range of Tyler standard screens employed in this procedure is used to show the effect of the air-jet attrition in changing the particle-size distribution of the coarser fractions of catalyst. Particularly in evaluating a new catalyst, it is significant to show the manner of breakdown in the coarser size range which results in the observed increase in -325-mesh fines.

During the screening procedure the moisture content of the catalyst changes to an extent depending on the level of catalyst activity, previous heat treatments, and exposure to atmospheric humidity. It is therefore necessary to correct the weight of the sample and the weights of the screen fractions to a constant moisture basis before calculation of the -325-mesh fraction by difference. Total volatile content at 2200° F. is determined on the sample before screen analysis and on the combined screen fractions.

Reproducibility of screen analyses is checked periodically to avoid varying precision of results. Frequent checks with the set of screens currently used are made on a standard catalyst sample to detect deterioration of the screens or errors in procedure. When it becomes necessary to replace worn screens, results with the new set are compared with previous results on the standard sample and with analyses with a set of reference screens. Variations between duplicate analyses with a single set of screens seldom exceed ±1 weight %. Because measurement of attrition is based on the difference between two analyses with the same set of screens, small variation in absolute values among different sets of screens has a minor effect on the calculated attrition rate.

No significant catalyst attrition to form -325-mesh fines has been found during the normal Ro-Tap screening procedure. Therefore, no corrections are needed to obtain the true particle-size distribution by screen analysis.

Roller Analyses. The present discussion is concerned only with measures taken to improve the accuracy of data obtained by the Roller analysis (2). To minimize the electrostatic effects shown by Matheson (2), the air supply is humidified by bubbling through a 38 weight % sulfuric acid solution. A constant air rate of 9.6 liters per minute is used in all analyses, based on a particle density of 1.35 grams per cc. In the absence of consistent data on particle density, no correction for the lower particle densities of the fresh catalysts has been made. Experience indicates, however, that such a correction would amount to less than 1 weight % decrease in each of the three finest size fractions.

In order to minimize attrition of catalyst particles during the Roller analysis, a modified aeration tube similar to that described by Matheson (2) has been employed.

DISCUSSION OF TEST

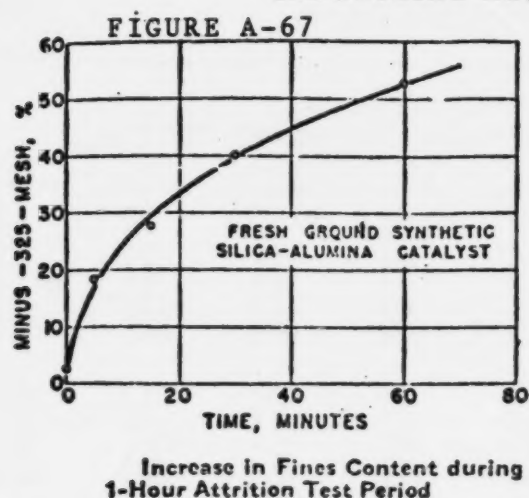
Information on the test variables that affect the proper interpretation of test results leads to a better understanding of the relation of the laboratory test to attrition conditions in a commercial

TABLE A-60

Effect of Catalyst Fines Content on Attrition
(Fresh-ground silica-alumina catalyst B)

Screen Analysis	Change to Attrition Test			
	As Received		Fines-Free	
	As received	After attrition	As received	After attrition
+ 80 mesh, %	0.6	0.2	0.8	0.2
- 80 + 100 mesh, %	2.5	0.4	4.9	0.6
- 100 + 150 mesh, %	19.1	7.3	31.3	10.0
- 150 + 200 mesh, %	22.2	14.5	32.9	19.0
- 200 + 270 mesh, %	12.1	10.8	17.9	11.4
- 270 + 325 mesh, %	6.9	4.6	9.4	6.0
- 325 mesh, %	26.6	62.2	2.8	52.8
	100.0	100.0	100.0	100.0
Increase in % of -325 mesh		35.6		50.6
Attrition rate, %/hour				
Increase in % of -325 mesh X 100		40.6		51.5
% +325 mesh in charge				

-A340-



cial unit and provides knowledge of the actual attrition mechanism.

Screen-analysis data show that the attrition obtained in the laboratory test in nearly all cases results in a net increase only in the -325-mesh fraction. Attrition-test data in Table I for an as-received fresh-ground silica-alumina catalyst show that the increase in the -325-mesh fraction from 36.6 to 62.2% resulted from a net decrease in all the coarser fractions. On the screen-analysis basis, therefore, the extent of attrition of -325-mesh particles already present in the sample to be tested is not measured. Particles finer than 325-mesh are termed fines in subsequent discussions.

Fines Content of Catalyst. The presence of fine particles in the catalyst tested is one of the most significant factors influencing attrition. The fines tend to cushion the impact of attrition of the coarser particles in two ways: by a cushioning effect which limits the force of collision impact between coarse particles, and by dilution which reduces the number of coarse particles available for attrition. The significance of these effects is illustrated by Table I. An attrition test with fresh-ground silica-alumina catalyst resulted in an increase in -325-mesh fines from 36.6 to 62.2%. When most of the fines had been screened from the catalyst before testing, there was an increase in -325-mesh from 2.8 to 52.8%.

It has been found possible to compensate for the dilution effect in an empirical manner by dividing the increase in -325-mesh material by the percentage of coarser than -325-mesh particles present in the test sample. Similar corrections may be applied to Roller-analysis data. When the data in Table I are corrected to this fines-free charge basis, the as-received sample shows an increase of only 40.4%, compared to 51.5% for the sample which was initially nearly free of fines. The calculation to a fines-free charge basis therefore does not completely correct for the total effect of the fines on attrition rate. It is believed that this difference is largely attributable to the cushioning effect of the fines.

Because it does not seem likely that any simple additional adjustment for fines would properly correct for the cushioning effect, which may vary from one type of catalyst to another, no further correction has been undertaken. However, as long as different catalysts are compared on the basis of similar fines contents, this deviation should not interfere with the usefulness of the test results nor the validity of such comparisons. In all cases, the previous correction of the breakdown to a fines-free sample basis has been employed. This corrected increase in -325-mesh is implied in this paper when the term attrition rate is used.

The fines formed during the attrition test tend to reduce the breakdown rate in the same manner as the fines present in the original charge, through an additional cushioning effect and a further decrease in the proportion of coarse particles available for attrition. In any given commercial unit the cushioning effect is

kept reasonably constant by the loss of fines to some equilibrium value. The inventory of coarse particles is maintained by additions of fresh catalyst. No attempt has been made in this batch test method to duplicate these characteristics of a continuous process. In an analysis of the laboratory test data for correlation with commercial operations these differences should be borne in mind.

Length of Test Period. Under the conditions of this test, the rate of catalyst breakdown decreases with the time the catalyst is subjected to the air jet. In Figure 2, the -325-mesh content of sample B is plotted against 5-, 15-, 30-, and 60-minute intervals of jet action. During the initial 5 minutes the -325-mesh increased from 3 to 19%, whereas during the last 5 minutes of the 60-minute test the increase was only from about 51 to 53%. The decrease in attrition rate with time is due to increase in attrition resistance of the particles as the rough edges are smoothed off, elimination of the weaker particles, increase in the amount of fines, which causes the cushioning effect previously discussed, and decrease in the number of coarse particles subject to attrition.

The relatively low breakdown rate after 60 minutes of jet action indicates that this is a suitable length of time for the test period. If the period were much shorter, the smaller amount of breakdown could not be measured so precisely; a longer test period would give only a small additional amount of attrition and would tend to reduce the contrast with a more attrition-resistant catalyst whose extent of breakdown would eventually more closely approach that of the weaker catalysts. As the attrition resistance of this ground silica-alumina catalyst is in the same range as other catalysts of commercial importance, the time period of the test is suitably oriented.

The decrease in attrition rate of this ground catalyst with time of jet action is more clearly shown for catalyst B in Figure 3. The fines-free silica-alumina catalyst in the first hour attrition period gave an increase of 53.1% in -325-mesh. The fines were then screened from the product and the coarse material was subjected to a second hour of attrition. Breakdown occurred at a rate of only 27.3% in this second hour. After another screening for removal of fines, a third hour of attrition showed a further decrease in breakdown rate to 21.1%. Microscopic examination of the products of these attrition tests showed that the originally sharp and irregular surfaces of the ground catalyst had been worn down until the edges appeared smooth and rounded like those of used catalyst withdrawn from a commercial unit. As the particle surfaces are rounded and weak particles eliminated, the attrition resistance of the remaining catalyst particles is significantly greater. This effect of mechanical action in the increase in attrition resistance is shown below for operations in commercial units.

Precision of Test Data. The range of variation in the data from different attrition tests on the same catalyst is not appreciably

TABLE A-61 NOT REPRODUCIBLE

Precision of Attrition Test Data						
(Microspheroidal spray-dried silica-alumina catalyst 7)						
Screen analysis	Catalyst as Received	Catalyst after Attrition				
		Attrition Test No.				
		56	110	112	122	151
+ 80 mesh, %	0.4	0.3	0.4	0.2	0.4	0.4
- 80 + 100 mesh, %	1.5	0.7	0.8	0.8	0.9	0.9
- 100 + 150 mesh, %	11.9	6.7	6.4	6.4	6.9	6.5
- 150 + 200 mesh, %	20.2	13.0	12.9	12.2	13.6	12.2
- 200 + 270 mesh, %	13.8	11.0	11.1	10.7	11.7	11.2
- 270 + 325 mesh, %	7.9	8.4	7.9	6.7	6.5	6.9
- 325 mesh, %	44.3	59.9	60.3	63.0	60.0	62.0
	100.0	100.0	100.0	100.0	100.0	100.0
Increase in % of -325 mesh		15.6	16.2	18.7	15.7	17.7
Attrition rate, %/hour		28.0	29.1	33.6	28.2	31.8
Test conditions						
Air rate, standard cu. ft./min.	0.25	0.25	0.25	0.25	0.25	0.25
Test period, minutes	60	60	60	60	60	60
Orifice pressure drop, lb./sq. inch	58	56	53.5	55.5	55	55
Test recovery, % chg.	93.0	97.9	97.9	96.9	97.4	97.4
Fines in filter, gram	0.2	0.1	0.5	0.5	0.6	0.6

Attrition of Fresh Ground Cracking Catalysts

Screen Analysis	Synthetic Catalyst		Natural Catalyst	
	Silica-Alumina A	Silica-Magnesia C	Catalyst E	Catalyst F
	As received	After attrition	As received	After attrition
+ 80 mesh, %	0.4	0.0	4.7	3.1
- 80 + 100 mesh, %	2.2	0.2	3.8	2.3
- 100 + 150 mesh, %	18.8	4.9	11.9	6.2
- 150 + 200 mesh, %	27.5	15.8	13.6	6.2
- 200 + 270 mesh, %	13.8	11.9	9.8	4.5
- 270 + 325 mesh, %	6.3	6.4	6.4	3.4
- 325 mesh, %	30.8	60.8	49.8	74.3
	100.0	100.0	100.0	100.0
Roller Analysis				
0-10 micron, %	4.3	19.4	4.0	20.8
10-20 micron, %	5.5	11.2	8.4	23.5
20-40 micron, %	11.9	16.8	16.6	16.7
40-80 micron, %	30.3	27.4	30.9	17.0
80+ micron, %	48.0	25.2	40.1	22.0
	100.0	100.0	100.0	100.0
Attrition Breakdown				
I. Increase in % of -325 mesh	30.0	22.2	34.5	18.6
Attrition rate, %/hour	43.4	35.5	48.8	36.0
II. Increase in % of 0-40 micron	23.7	23.6	22.0	19.3
Increase in % of 0-40 micron $\times 100$	32.8	30.5	45.1	36.3
% 40+ micron in charge				
III. Increase in % of 0-20 micron	20.8	17.3	31.9	18.9
Increase in % of 0-20 micron $\times 100$	23.1	19.2	36.4	21.3
% 20+ micron in charge				

TABLE A-62

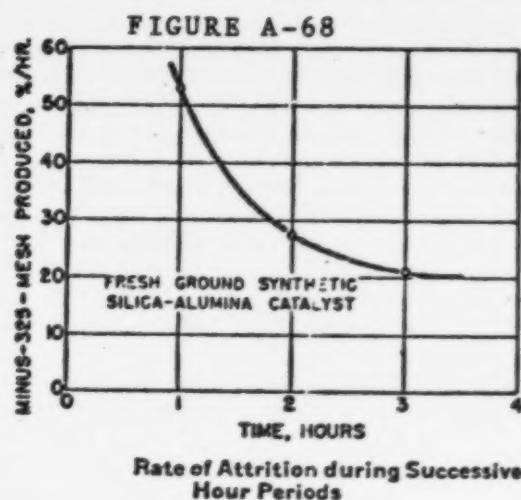
greater than the variation to be expected from the screen analyses. Data from a series of tests on a microspheroidal silica-alumina catalyst (Table II) show the typical range of deviation. The increase in -325 mesh varied from 15.6 to 18.7%, for a maximum variation in attrition rate from 28.0 to 33.6%. This range represents a variation of 2.0%. The test conditions have been included in Table II to show when normal variations

two samples of a natural clay catalyst are presented in Table III. The screen analyses on the silica-alumina catalyst sample show an increase in -325 mesh from 30.8 to 60.8% for an attrition rate of 43.4%. The silica-magnesia catalyst shows a somewhat better resistance to breakdown than the silica-alumina, with an attrition rate of 35.5%. Natural catalyst sample E shows a decrease in -325 mesh from 49.8 to 74.3% for an attrition rate of 48.8%; catalyst F was very close to silica-magnesia, with an attrition rate of 36%. The difference in breakdown shown by the two natural catalysts may result from variations in the quality of the raw material.

The general trend of catalyst particle-size distribution obtained in the laboratory attrition test, shown in Table I, may also be seen from the screen-analysis data in Table III. The net increase in fine material due to particle breakdown is practically all in the finest size fraction; only the silica-magnesia shows any increase in the 270- to 325-mesh material. The trend is further shown by the Roller-analysis data of Table III, where most of the increase in fine material occurs in the 0- to 10-micron fractions, a lesser amount in the 10- to 20-micron fractions, and still less in the 20- to 40-micron fractions. For the silica-alumina catalyst this amounts to increases of 15.1, 5.7, and 4.9%, respectively, for these three fractions.

The material finer than 20 microns produced in the laboratory attrition test is of particular significance from the standpoint of catalyst losses from a commercial unit having no Cottrell precipitator; all particles finer than about 20 microns are rapidly lost from such a unit. A comparison of the ground catalysts on this basis shows the same relative attrition resistances as shown by the screen-analysis data.

The attrition rates in Table III, based on screen analyses, are considerably higher than the corrected increases in 0- to 40-micron material as determined from Roller analyses. The principal reason for this deviation is that the -325-mesh screen fraction is considerably greater, in comparison to the 0- to 10-micron fraction, than would be indicated by the nominal screen mesh size (44 microns). This larger -325-mesh fraction results from passage of particles considerably larger than 44 microns through the 325-mesh screen, which was shown by microscopic examination. With its higher initial fines content, the screen analysis consequently provides a greater correction when calculated to a fines-free charge basis. However, the deviation of screen-analysis data from the Roller data does not limit the usefulness of relative



The amount of breakdown obtained in the laboratory test is not significantly affected by variations in orifice pressure drop caused by reasonable variations in the accuracy of drilling the $\frac{1}{16}$ -inch hole. Results obtained with plates giving pressure drops as high as 65 pounds per square inch have not shown any significant difference from the data for 55 to 58 pounds per square inch in Table II. Hence, test results from different sets of apparatus may be expected to be in good agreement.

ATTRITION RESISTANCE OF FRESH CATALYSTS

Ground Catalysts. Samples of the three principal commercial types of fresh-ground cracking catalyst have shown about the same range of attrition resistance in the laboratory test. Data on particle-size distribution before and after attrition of a synthetic silica-alumina catalyst, a synthetic silica-magnesia catalyst, and

TABLE A-63

Attrition of Fresh Microspheroidal Cracking Catalysts

Attrition Breakdown	Silica-Alumina		Silica-Magnesia	
	G*	H*	J*	K*
I. Increase in % of -325 mesh	13.5	9.0	36.9	18.3
Attrition rate, %/hour	27.0	17.7	60.9	20.4
II. Increase in % of 0-80 micron	..	..	..	22.8
Increase in % of 0-80 micron X 100	..	..	..	31.8
% 80+ micron in charge	..	..	..	..
III. Increase in % of 0-40 micron	13.4	2.7	31.4	15.7
Increase in % of 0-40 micron X 100	18.8	2.8	40.1	17.0
% 40+ micron in charge	..	..	..	..
IV. Increase in % of 0-20 micron	11.6	1.5	14.5	9.2
Increase in % of 0-20 micron X 100	12.7	1.5	14.9	9.5
% 20+ micron in charge	..	..	..	..

* Spray dried catalyst.

* Oil-dropped catalyst.

comparisons among screen analyses as employed in the present method.

Microspheroidal Catalysts. Samples of some microspheroidal catalysts have shown considerably better attrition resistance than ground catalysts in the laboratory attrition test. Data in Table IV on spray-dried silica-alumina microspheroidal catalyst sample G show an attrition rate of 27.0%, compared to the 43.4% shown in Table III for ground silica-alumina catalyst A. There is a corrected increase in 0- to 20-micron material of 12.7% for this microspheroidal catalyst, while the ground silica-alumina shows 23.1%. An oil-dropped microspheroidal silica-alumina catalyst, sample H, gives an attrition rate of 17.7%; on the Roller-analysis basis the breakdown is even less, with an increase of only 1.5% in the 0- to 20-micron fraction.

The large difference in the amount of breakdown shown by screen and Roller data for sample H illustrates an effect of original particle-size distribution upon the measurement of attrition rate. If a large proportion of particles of a catalyst is close to the 325-mesh—a relatively small change in size of these particles could be reflected in a markedly higher attrition rate than would be the case for an originally coarser sample. Over 60% of the particles of sample H were in the 40- to 80-micron range; therefore the 325-mesh screen which has a cut point within this range, will show a greater amount of attrition than indicated on the Roller basis. Other catalysts had more uniform and mutually similar initial particle-size distributions, so that this effect was not an important factor.

Excessive amounts of agglomerated particles in a microspheroidal catalyst can have a highly detrimental effect on its attrition resistance. The agglomerates break apart under attrition conditions much more readily than the spheres themselves; hence, if the agglomerates are composed of fine particles, the over-all attrition resistance can decrease into the range for ground catalysts. An example of this condition is the case of sample J. (Table IV). This shows an attrition rate of 60.9%, which is greater than that for any of the ground catalysts in Table III. The increase in 0- to 20-micron material is not so great as for a ground

catalyst in proportion to the increase in -325 mesh, as half of the particles resulting from breakdown of agglomerates were in the 20- to 40-micron range. The corrected increase of 14.9% 0 to 20 microns nevertheless approaches the 10.2% shown for catalyst C.

Microscopic examination of the original catalyst showed individual particles to be spherical in shape, but practically all the particles in the 80- to 200-mesh range and over 50% in the 200- to 325-mesh range were agglomerates. During the attrition test, these agglomerates were largely broken down; the resulting finer fractions were composed practically completely of individual spheres. This showed that the high proportion of fine particles in the agglomerates making up this batch of microspheroidal catalyst did not permit it to have the desired advantages of attrition resistance over a ground catalyst.

The data on sample K (Table IV) show better attrition resistance than for sample J. The attrition rate decreased to 20.4% because of the presence of fewer agglomerates. Although there were considerable proportions of agglomerates in the coarser fractions, these were made up of larger particles. The data in Table IV show increases of 9.2% in 0 to 20 microns, 15.7% in 0 to 40 microns, and 22.8% in 0 to 80 microns. It follows that the fine material formed during attrition consisted of about 40% 0 to 20 microns, 30% 20 to 40 microns, and 30% 40 to 80 microns.

Attrition Resistance of Heat-Treated Fresh Catalysts. The effect on attrition resistance of heating catalyst to operating temperature of the cracking unit varies with different catalysts and with the extent of previous calcinations. In Table V are presented data on samples of various types of catalyst which, before testing, were heated at 1100° F. for 4 hours in a muffle furnace. A comparison of the data for ground silica-alumina catalyst A before and after heating shows a decrease in attrition rate from 43.4 to 42.1%. A similar comparison for the more attrition-resistant of the two samples of natural catalyst also indicates the heating to give a decrease in the attrition rate, from 36.0 to 31.7%. A similar but greater decrease in attrition rate occurred on heating ground silica-magnesia catalyst D and resulted in an attrition rate of 29.1% compared to 36.4% for the untreated catalyst.

With both the spray-dried and oil-dropped microspheroidal silica-alumina catalyst samples, however, no decrease in attrition rate occurred as a result of the heat treatment. Sample G had an attrition rate of 27.1% after heating, compared to the original value of 27.0%. The oil-dropped catalyst showed an increase in attrition rate from 17.7 to 20.4%.

On the basis of the Roller increase in 0- to 20-micron material from attrition, the breakdown of ground silica-alumina decreased from 23.1 to 18.1% as a result of the heating; this is a greater effect than was shown by screen-analysis data. The Roller data also show that the decrease in attrition rate from heating silica-magnesia sample D was great enough to give it a considerably lower rate than microspheroidal silica-alumina sample G, which had shown little change.

Such data on the attrition resistance of catalysts after heat treatment provide a clearer picture of possible effects occurring

TABLE A-64

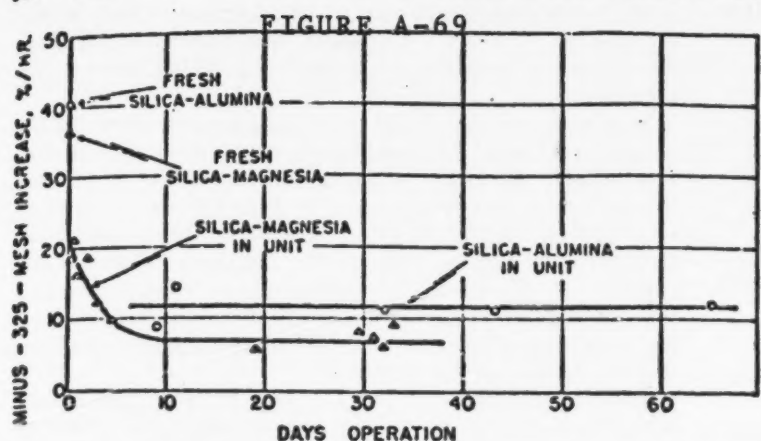
Attrition of Fresh Catalysts after Heating at 1100° F. for 4 Hours

Attrition Breakdown	Ground Catalyst								Microspheroidal			
	Silica-Alumina A		Silica-Magnesia D		Natural E		Natural F		Silica-Alumina Catalyst		Oil-Dropped, H	
	As received	Heated	As received	Heated	As received	Heated	As received	Heated	Spray-Dried, G	Heated	As received	Heated
I. Increase in % of -325 mesh	30.0	27.9	24.6	17.7	24.7	..	18.6	16.7	13.5	13.3	9.0	9.0
Attrition rate, %/hour	43.4	42.1	36.4	29.1	48.8	..	36.0	31.7	27.0	27.1	17.7	20.4
II. Increase in % of 0-40 micron	25.7	19.0	15.9	8.7	32.6	..	19.3	10.6	13.4	11.0	2.7	3.5
Increase in % of 0-40 micron X 100	32.8	24.9	21.1	11.7	45.1	..	26.3	15.5	18.8	15.3	2.8	3.6
% 40+ micron in charge	..	..	..	..	..	..	..	..	..	..	..	..
III. Increase in % of 0-20 micron	20.8	16.3	12.5	6.0	31.1	..	18.1	11.1	11.6	10.8	1.5	2.7
Increase in % of 0-20 micron X 100	23.1	18.1	14.3	6.8	36.4	..	21.3	12.9	12.7	11.6	1.5	2.8
% 20+ micron in charge	..	..	..	..	..	..	..	..	..	..	..	..

NOT REPRODUCIBLE

June 1949

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Decrease in Attrition Rate of Ground Catalysts during Operation of Commercial Fluid Unit

in a cracking unit, even though the much more rapid heating which occurs when fresh catalyst is added to a unit may have a somewhat different effect. On the other hand, inasmuch as significant attrition of a fresh catalyst may occur before heating to cracking temperature during the charging of fresh catalyst to a commercial unit, attrition characteristics of catalyst samples both before and after heating should be considered in the evaluation of a new catalyst.

ATTRITION RESISTANCE OF USED CATALYSTS

The attrition of a fresh-ground cracking catalyst decreases rapidly during the initial period of operation in a commercial unit. Tests on samples of ground silica-alumina catalyst withdrawn during a commercial run. Before being charged to the unit, the fresh catalyst had an attrition rate of 40%, whereas the used catalyst from the unit showed a breakdown averaging only 12% over the first 2 months of the run.

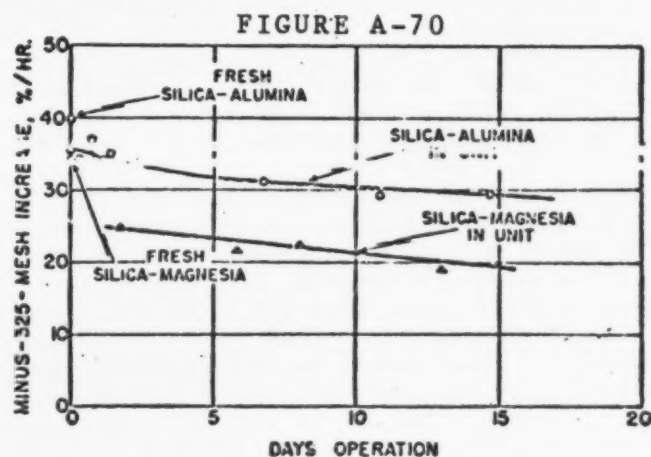
Similar data in Figure 4 from a run with a ground silica-magnesia catalyst show a large decrease in attrition rate during transfer of catalyst from the storage bin to the regenerator and before circulation of catalyst from the regenerator to the reactor had begun. The fresh catalyst from the bin showed an attrition rate of 36%, whereas that in the regenerated-catalyst standpipe at the start of transfer of catalyst to the reactor showed a rate of only about 20%. There appear to be three factors contributing to the rapid increase in attrition resistance before the start of normal cracking operations: passage of catalyst through the line from the storage bin to the unit, aeration in the unit, and heat. The attrition rate of this catalyst decreased further during the first 2 weeks of operation until later samples showed a breakdown of less than 10% under the attrition-test conditions. Differences in operating conditions between the commercial-unit runs with these two catalysts do not permit an exact comparison of their attrition resistance at equilibrium in a unit.

The larger part of the decrease in attrition rate shown by these ground catalysts during commercial-unit operation results from elimination of weak particles and the rounding-off of the rough, irregular particle surfaces by mechanical wearing. During operation in a fluid-cracking pilot plant in which erosion conditions were much less severe, the decrease in attrition rate of the ground silica-alumina and silica-magnesia catalysts was much less. The smaller extent of attrition in the pilot plant resulted from operation with lower transfer-line velocities and use of filters instead of cyclones for catalyst recovery. In Figure 5 are shown data from pilot-plant runs with fresh batches of the same catalysts that were used in the commercial unit. With silica-alumina catalyst, following an initial decrease in attrition rate from 40% for the fresh catalyst to about 36% at the start of the run, which represents the effect of temperature, there was a further decrease to

only about 29% after 2 weeks of operation. Because the pilot plant was operating under the same cracking process conditions as the commercial unit, which showed a decrease in attrition rate to 12%, it is concluded that exposure to heat and alternating reaction and regeneration cycles has relatively little effect on the attrition resistance of this catalyst. The decrease in attrition rate from about 36 to 12% in commercial-unit operation as a result of mechanical action is similar to the rapid decrease which was shown in Figure 3 to occur in the laboratory test.

The ground silica-magnesia catalyst showed a greater initial decrease in attrition rate in the pilot plant than did the silica-alumina, but considerably less than the decrease in the commercial operation. The laboratory attrition rate for silica-magnesia samples after 2 weeks of operation in the pilot plant was 19%, compared to about 7% for catalyst from the commercial unit. The greater effect of temperature

on the silica-magnesia catalyst is the explanation for its greater initial decrease in attrition rate. It can be estimated from extrapolation of the silica-magnesia curve in Figure 5 that the initial decrease in attrition rate from 35 to 25% corresponds to the initial effect of temperature. The decrease in attrition rate in the commercial unit from 25 to 7% would therefore represent largely the effect of mechanical action.



Decrease in Attrition Rate during Operation of Fluid-Cracking Pilot Plant

CONCLUSIONS

In a laboratory accelerated-attrition test for measuring the relative resistance to breakdown of fluid-cracking catalysts the catalyst is subjected to the action of a high-velocity air jet, and the amount of breakdown is determined by the change in particle-size distribution. Such data are useful in the estimation of relative loss rates in commercial operations.

The attrition resistances of fresh-ground commercial silica-alumina, silica-magnesia, and natural clay cracking catalysts are in the same range.

Microspheroidal catalysts show a considerably better attrition resistance than ground catalysts, because of their improved particle shape. The presence of agglomerates formed during manufacture can greatly reduce this advantage.

Heat treatment of fresh catalysts prior to attrition testing has a varying effect for different catalysts. The attrition resistance of the ground catalysts increased after heating at 1100° F., whereas that of the microspheroidal catalysts showed little change. Attrition data on heat-treated samples therefore provide a more realistic evaluation of new catalysts.

The attrition resistance of a ground catalyst improves greatly in the laboratory test as sharp edges and irregular surfaces are

rounded off and weak particles eliminated. The attrition causes a rounding off of sharp edges of particles similar to that occurring in a commercial fluid catalytic cracking unit.

The attrition resistance of ground catalysts increases rapidly during operation in a commercial unit. Mechanical erosion of particles is the primary cause of this increase. With a ground silica-magnesia catalyst the effect of process temperatures is significant.

The presence of fine particles in a catalyst reduces the attrition rate of the coarser particles, and a correction to a fines-free charge basis helps to compensate for this effect. The most valid comparisons of attrition resistance are obtained when the catalyst samples have comparable fines contents.

The particle size of the fine material produced during the attrition of a catalyst in the laboratory test is predominantly less than 10 microns with the exception of some agglomerated catalysts. The particle-size distribution resulting from the attrition of an agglomerated catalyst depends on the size of the individual particles in the agglomerates.

ACKNOWLEDGMENT

It is desired to acknowledge the development of this general test method by J. T. Clapp and J. B. Gray. Appreciation is also expressed for many helpful suggestions by A. L. Conn and J. O. Howe.

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- (6) Roller, P. S., U. S. Bur. Mines, *Tech. Paper* 490, 46 (1931).
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Received January 3, 1949.

APPENDIX B

EFFECTS OF OXYGEN AND WATER VAPOR ON SO₂ SORPTION

The following discussion, which is taken from the AVCO Final Report "Removal of SO₂ From Flue Gas", Contract No. PH86-67-51, dated November 1, 1967, appears to adequately describe the subject effects.

Effect of Moisture and Oxygen in the Flue Gas

A large amount of data was taken early in the program on the mistaken assumption that sorption rates were unaffected by the presence of water vapor in the flue gas. The assumption was based on a series of experiments which were apparently in error. All recent data, and the majority reported on here were taken with a flue gas containing 5-7 percent moisture by volume.

The effect of water vapor was demonstrated by sorptions S-51 through S-55 which were run at 300° C and about 1 percent SO₂. A 216 mg sample of Peter Spence sorbent was used. Run S-51 used dry flue gas and showed a weight gain of 15 mg after 100 minutes. Run S-52 used flue gas with 5.2 percent moisture and gained 96 mg in the same period. In S-53 the dry results of S-51 were replicated at a high oxygen concentration and slightly higher rates were

TABLE A-65
SUMMARY OF SORPTION DATA

Run No.	Sample	T(°C)	Gas Velocity (ft/sec)	Vol. Percent SO ₂ †	Vol. Percent H ₂ O **	Vol. Percent O ₂ †	Particle †† Diameter (in.)	Theoretical k _c (ft/hr)	k _c from data (ft/hr)	K from data (hr ⁻¹)	D from data (cm ² /sec)
S-47	5	300	.5	1.03	0	15.5	.120	505			
S-49	5	300	.5	est 1.0	0	3.6	.120	505			
S-51	6	300	.5	1.03	0	3.6					
S-52	6	300	.64	.83	5.2	16.6					
S-53	6	300	.5	est 1.0	0	21.0					
S-54	6	300	.66	0	7.2	0					
S-55	6	300	.64	.78	5.2	2.85					
S-62	9	300	7.3	.90	3.5	3.27	.102	1050	261		.012
S-63	9	300	1.9	.89	7.2	3.145	.102	1050	161		.024
S-64	9	300	1.9	.87	7.2	3.145	.102		117		.024
S-65	9	350	1.9	.95	7.2	3.145	.102		105		.014
S-67	9	200	1.9	.68	7.2	3.145	.102		103		.014
S-68	9	250	1.9	.87	7.2	3.145	.102		151		.0099
S-69	9	150	1.9	.91	7.2	3.145	.102		179		.012
S-70	9	350	1.9	.87	7.2	3.145	.102				
S-79	12	300	7.6	.81	7.2	3.15	.102	1460	179	139	.019
S-80	12	300	7.6	.96	7.2	3.15	.102	1460	171	118	.013
S-81	13	300	7.6	.85	7.2	3.15	.066	1880	148	332	.0062
S-82	13	300	7.6	.92	7.2	3.15	.066	1880	252	174	.0071
S-83	13	300	7.6	.81	7.2	3.15	.066	1880	145	197	.0085
S-85	14	300	7.6	.96	7.2	3.15	.079	1670	391	312	.012
S-86	14	300	7.6	1.02	7.2	3.15	.079	1670	498	442	.010

*, from pressure change on addition of O₂ to feed cylinder

† by chromatography

†† by sieving

** from humidifier temperature

observed. In S-54 the sorbent was exposed to a mixture containing 7.2 percent H₂O and 92.8 percent N₂ by volume. The weight gain was only 1 mg. The results of S-52 with moist flue gas were replicated in run S-55 at a low oxygen concentration. Sorption curves for each of these runs are given in Figures 25 and 26. Note in Figure 26 that raising the oxygen concentration from 2.8 percent to 16.6 percent had no effect on the sorption in moist flue gas.

Thus, increased concentration of O₂ gave slightly higher sorption rates in the absence of moisture in the gas, but there was no effect of oxygen content with moist gas.

An equal increase in rate over previous dry sorptions was observed with the W. R. Grace material. The effect of water vapor on W. R. Grace sorbent can be seen by comparing runs S-49 (dry, 300° C) with S-79 (7.2 percent moisture, 300° C). The sorption curves are presented in Figure 27 and clearly show the increase in sorption rate in the presence of moisture.

The mechanism by which water vapor accelerates the sorption is not understood. The rate of the surface sorption reaction may be catalyzed by the presence of water. Alternately, capillary condensation of the moisture might allow rapid sorption of SO₂ in the condensed water. A third possibility is that a surface diffusion mechanism might be activated by absorbed water.

The possibility of capillary condensation may be checked with the Kelvin equation which relates vapor pressure lowering to the radius of curvature of a curved surface.*

$$\ln \frac{p_0}{p} = \frac{2 \gamma}{r \rho} \frac{M}{RT}$$

where

- p_0 = vapor pressure of water at T
- p = partial pressure of H₂O in gas phase
- γ = surface tension of water at T
- ρ = density of condensed liquid
- R = gas law constant
- M = molecular weight of condensed liquid
- T = temperature
- r = pore radius

* Glasstone, Textbook of Physical Chemistry, van Nostrand, Princeton, N.J. (1946) p. 493.

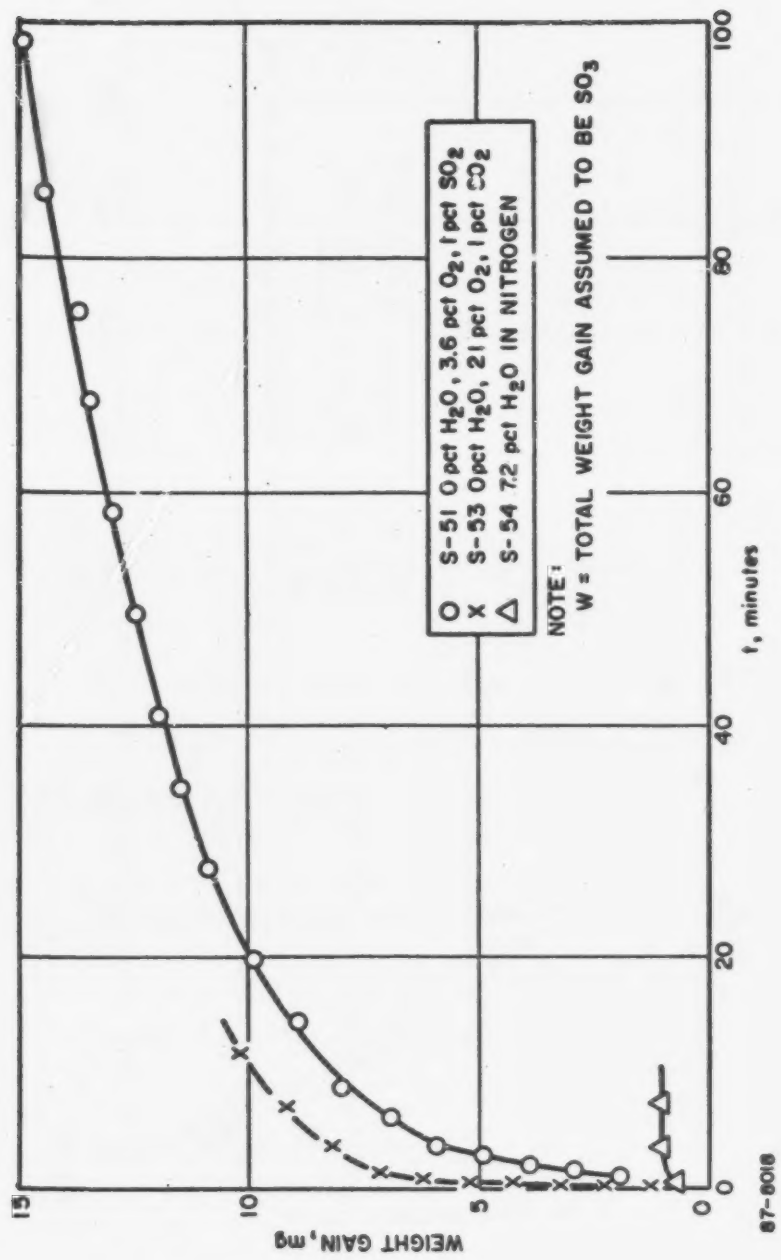


FIGURE B-71 SORPTION DATA FOR SAMPLE NO. 6

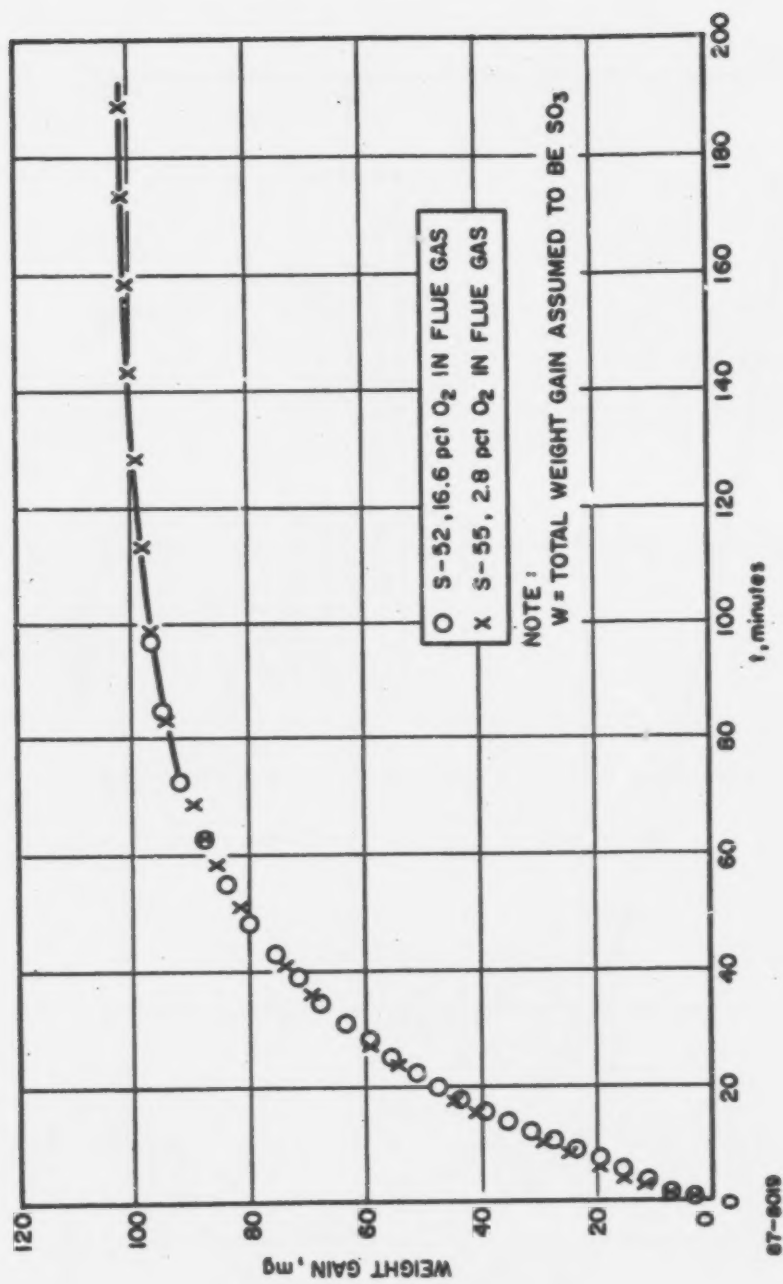


FIGURE B-72 - SORPTION DATA FOR SAMPLE NO. 6

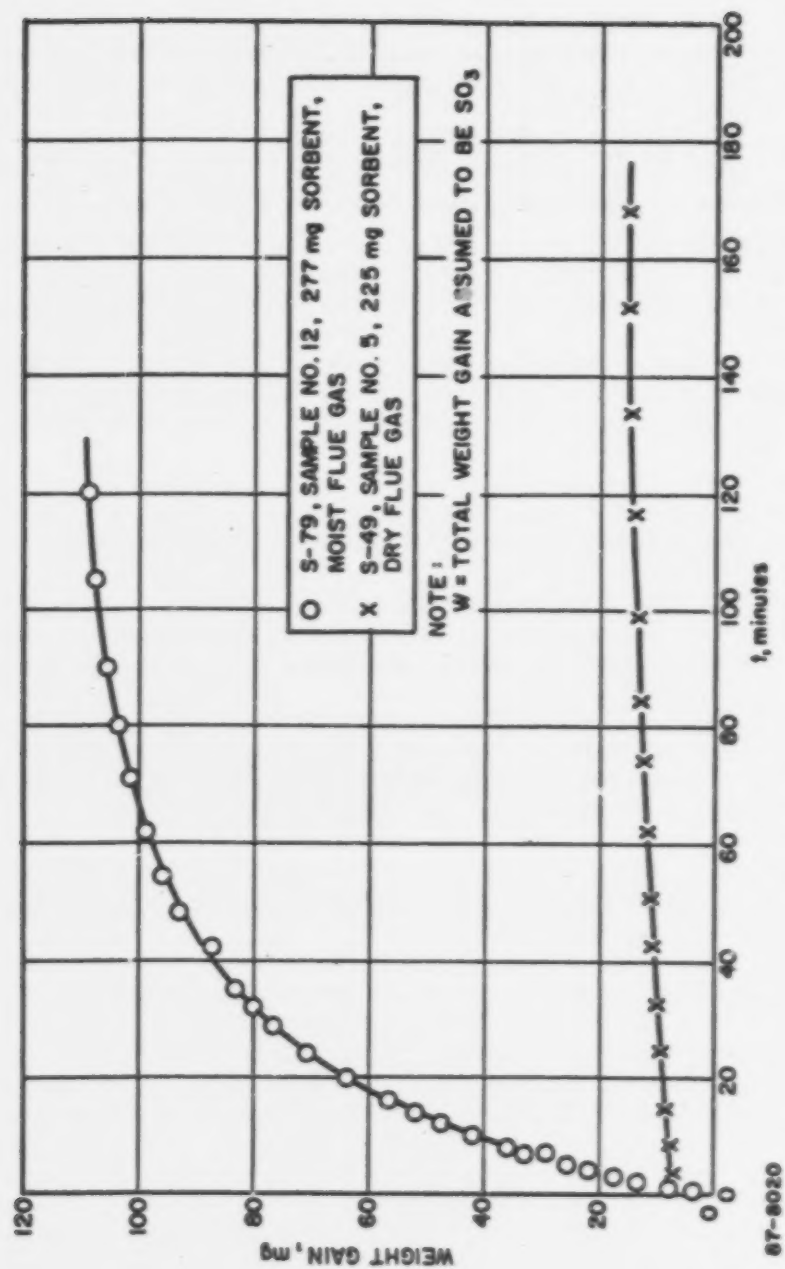


FIGURE B-73 - SORPTION DATA FOR WET AND DRY FLUE GAS

The maximum pore radius which could support capillary condensation of moisture was computed using typical sorption conditions.

TABLE B-66

$T(^{\circ}K)$	p_o (atm)	p (atm)	$\rho \left(\frac{gm}{cc} \right)$	$\gamma \left(\frac{dyne}{cm} \right)^*$	$r \left(\overset{\circ}{A} \right)$
423 (150° C)	4.70	.072	1.0	47	1.2
573 (300° C)	84.8	.072	1.0	20	0.21

The concept of capillary condensation in pores of one molecular diameter is not sensible. As a result capillary condensation is probably not the explanation of the high sorption rate in the presence of moist flue gas.

Alternately, sorbed moisture might provide a path for surface diffusion of SO_2 on the pore walls. If this were an important factor, it could be checked by stopping the sorption periodically by sweeping the sorption chamber with N_2 . In the presence of N_2 the surface diffusion would be expected to continue causing a levelling of the sorbate concentration profile. Restoring the sorption should result in a different rate than previous to standing in N_2 due to the redistribution of the sorbate within the particle.

All sorptions from S-78 on have been run on an intermittent basis. Sorption was carried out for a given time, then the sample chamber swept with nitrogen and the sample weighed in static nitrogen. Sorption was then resumed in

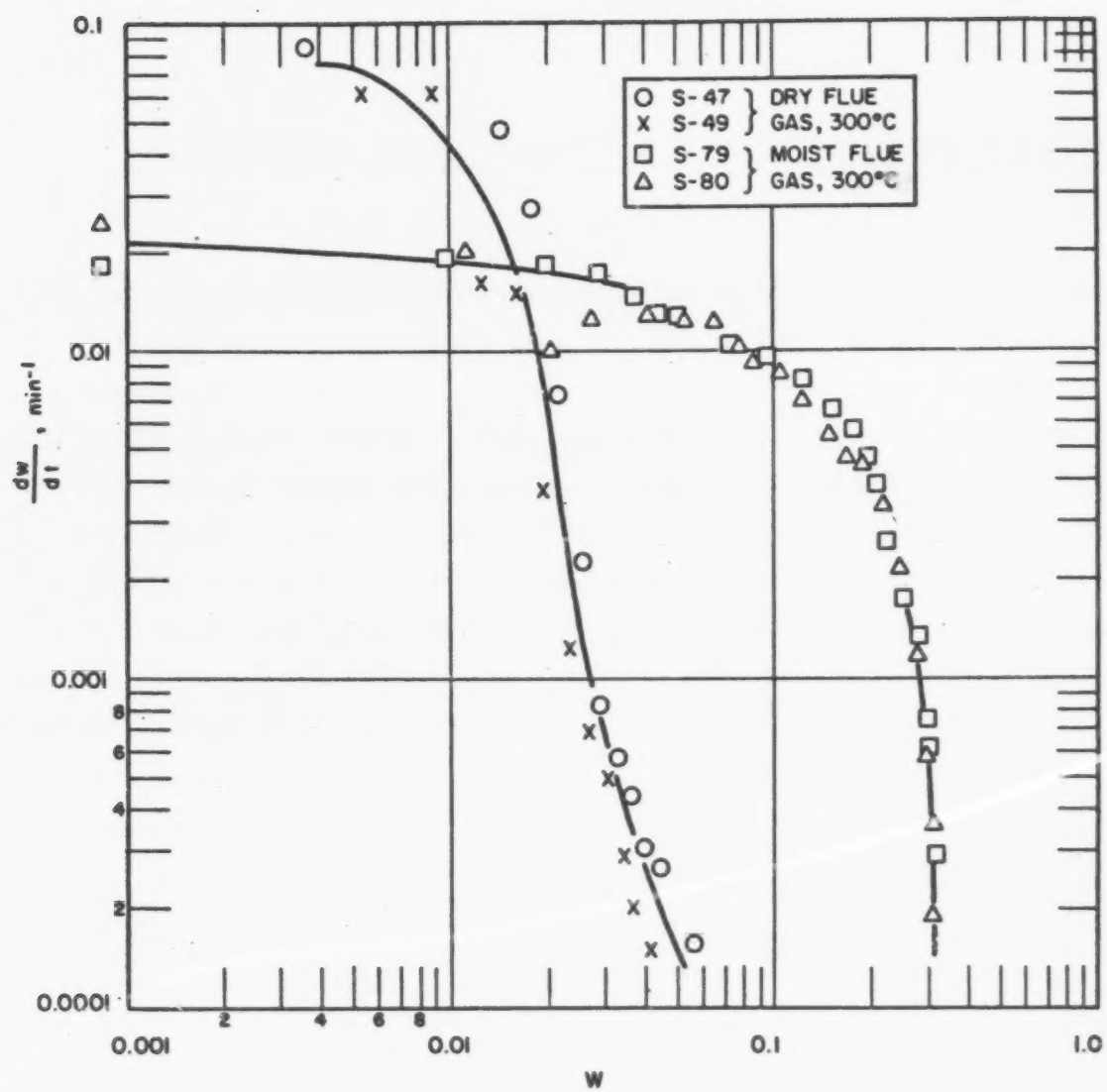
been continuous. There are no evident differences in the sorption curves or diffusivities obtained in the diffusion controlled region (high loading region) of the sorption. This observation suggests that surface diffusion is not a large contributor to the total diffusion process.

By elimination, the implication is that moisture catalyzes the sorption step at the sorbent surface but this conclusion is by no means based on adequate testing.

The rate of sorption curve, given in Figure 28, indicates that there is a large effect of moisture on the sorption rate at loadings greater than two percent of saturation. However, there was no increase in the initial rate when moisture was added. In fact, the data show a decrease, but this may not be significant in light of the poor resolution of initial rates by these experiments.

The moisture levels used, 5.2 percent and 7.2 percent, are similar to those found in actual flue gas. In the region where pore diffusion is controlling, higher moisture content should not affect the sorption rate. The mechanism of the initial rate is not known, nor is the effect of water content on this rate known exactly.

Estimated from values given at temperatures up to 100° C.



87-8021

FIGURE B-74 - SORPTION RATE DATA, W.R. GRACE SORBENT

APPENDIX C

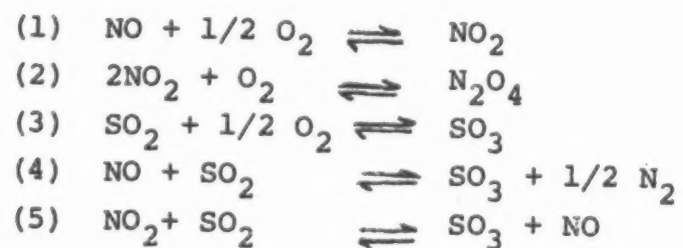
NITROGEN OXIDE CHEMISTRY - THERMODYNAMIC CALCULATIONS

The following discussion of nitrogen oxide chemistry was presented by the W. R. Grace Co. in the September 1968 monthly report, Contract No. PH-86-67-129. It is included here since 1) it shows some of the reactions that might occur during sorption of SO_2 by alkalized alumina, and 2) Grace developed these calculations in support of their theory of absorption. Although the exact mechanism by which sorption of SO_2 from stack gases occurs has not been agreed upon by all investigators, Grace's theory (i.e., oxidation of SO_2 to SO_3 is substantially accelerated by NO_x and the resulting SO_3 reacts rapidly with the basic surface sites on the alkalized alumina) is certainly a distinct possibility.

W. R. Grace Discussion

The stack gases from which sulfur dioxide is absorbed by alkalized alumina contain oxides of nitrogen. In order to substantiate the postulated theory of absorption, it became necessary to identify the state of oxidation of nitrogen. The data summarize the thermodynamic equilibrium considerations, and a discussion of the thermodynamic feasibility of some of the probable reactions is presented.

The reactions considered are:



The standard free energies of reaction for the temperature range 300°K(80°F) to 700°K(800°F) for these five reactions are given in the attached data sheets, one through five respectively. Data sheet six shows the concentrations of components when reaction #(1) is superimposed on reaction #(5) at equilibrium at 600°K (620°F).

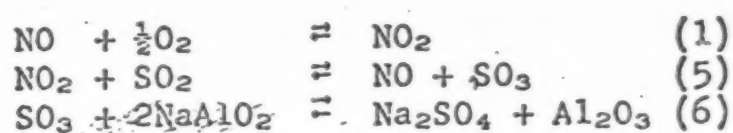
The assumptions of ideal components and ideal mixtures were made in the calculations. The flue gas at one atmosphere was assumed to contain 5% O₂, 0.05% mole equivalent of nitric oxide (NO) and 0.3% sulfur dioxide (SO₂), the balance being inert gases.

The thermodynamic considerations predicted that when the stack gases contain 5% oxygen and 0.05% nitric oxide (NO), it is possible that equilibrium exists between nitric oxide and nitrogen dioxide (NO₂). At 700°K (800°F) 0.015% nitric oxide can come to equilibrium with a maximum 0.035% nitrogen dioxide.

Dimerization of nitrogen dioxide to dinitrogen tetroxide is thermodynamically not feasible between 400°K (260°F) and 700°K (800°F). However, it can take place below 325°K (125°F).

In the temperature range considered, reactions # (4) and # (5) are feasible. The high negative value for the standard free energy of reaction of # (4) as compared to # (5) does not necessarily predict that # (4) is favored to take place. It merely indicates that the reaction # (4) at equilibrium is probably more complete than reaction # (5) at the same temperature and equivalent concentrations.

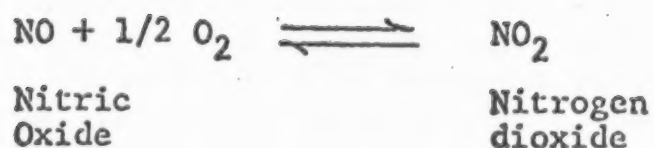
Based on the above information the following sequence of steps for the absorption of SO_2 was considered.



Attempts were made to superimpose the two gas phase reactions involved in the above sequence of steps. It was assumed that at 600°K (620°F), reaction # (1) attains equilibrium and the concentrations of NO 0.0037% and of NO_2 0.0463% were assumed to be the initial concentrations of the respective gases for reaction # (5). Sulfur dioxide concentration of 0.3% was assumed. Equilibrium analysis of reaction # (5) under these conditions at 600°K (620°F) indicates that the forward reaction is 99.9% complete. The equilibrium concentrations of the components of the reaction mixture assuming ideal gases and ideal mixture are shown below.

		<u>Mole %</u>	<u>Vol %</u>
$[\text{NO}_2]$	=	0.01%	.005
$[\text{SO}_2]$	=	72.6%	.254
$[\text{NO}]$	=	14.2%	.050
$[\text{SO}_3]$	=	13.2%	.046

It must be noted that the above calculations are based on thermodynamics only. The actual occurrence of any of these reactions will be governed by the kinetics of the competing or series reactions.

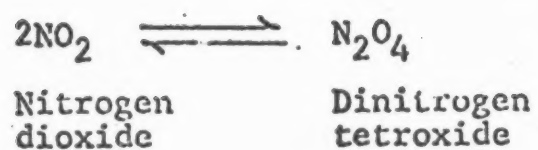


- Assumptions:
- (1) Ideal gas and ideal mixture
 - (2) Stack gas containing 0.05% mole equivalent of NO and 5% oxygen at 1 atmosphere

Reference: JANAF Thermochemical Tables

Temp. °K	Temp. °F	Std. Free Energy of Reaction ΔF° kcals/mole	Equilibrium Constant K	X %
300	80	-8.4	4300	100
400	260	-6.6		
500	440	-4.8		
600	620	-3.0	12.56	93
700	800	-1.2	0.37	70

- Conclusions:
- (1) The forward reaction is feasible in the temperature range.
 - (2) Thermodynamically at 300°K, it is possible that the state of oxidation of nitrogen is completely nitrogen dioxide (NO₂) and at 700°K, equilibrium may exist for the stack gases to contain 0.035% nitrogen dioxide (NO₂) and 0.015% nitric oxide (NO).



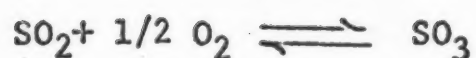
Assumption: Ideal gas and ideal mixture

Reference: JANAF Thermochemical Tables

Temp. °K	Temp. °F	Std. Free Energy of Reaction ΔF° kcals/mole
300	80	-1.1
400	260	+3.1
500	440	+7.2
600	620	+11.3
700	800	+15.4

Conclusions: By interpolation, the forward reaction is feasible at temperatures less than 325°K or 125°F.

Data Sheet (3)



Reference: International Critical Tables Vol. 7, page 236

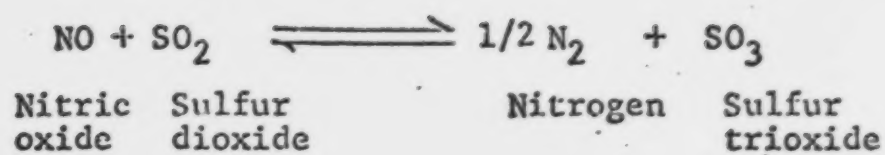
ΔF° = Standard Free Energy of Reaction, kcals/mole
 = $-22.6 + 0.02136 T$ at T °K.

Temp. °K	Temp. °F	Std. Free Energy of Reaction ΔF° kcals/mole	Std. Free Energy of Formation of SO_2^* ΔF° kcals/mole	Std. Free Energy of Formation of SO_3^* ΔF° kcals/mole
300	80	-16.2	-71.7	-87.9
400	260	-12.1	-71.9	-84.0
500	440	-11.9	-71.9	-83.8
600	620	-9.8	-71.8	-81.6
700	800	-7.6	-71.6	-79.2

*Reference - JANAF Thermochemical Tables.

** $\Delta F^\circ_{\text{SO}_3} = \Delta F^\circ_{\text{SO}_2} + \Delta F^\circ_{\text{Reaction}}$

Conclusion: The forward reaction is feasible in the temperature range..



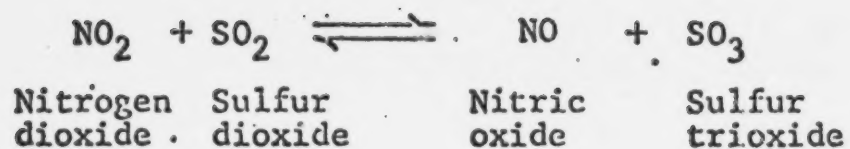
Assumption: Ideal gas and ideal mixture

Reference: (1) JANAF Thermochemical Tables
 (2) Data Sheet (3)

Temp. °K	Temp. °F	Std. Free Energy of Reaction ΔF° kcal/mole
300	80	-36.9
400	260	-32.5
500	440	-32.0
600	620	-29.6
700	800	-27.1

Conclusions: The forward reaction is feasible up to almost completion in the temperature range considered.

Data Sheet (5)

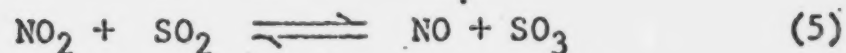
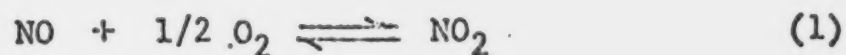


Assumptions: Ideal gas and ideal mixture.

Reference: (1) JANAF Thermochemical Tables
 (2) Data Sheet (3)

<u>Temp. OK</u>	<u>Temp. OF</u>	<u>Std. Free Energy of Reaction ΔF° kcals/mole</u>
300	80	-7.8
400	260	-7.4
500	440	-7.1
600	620	-6.8
700	800	-6.5

Conclusions: The forward reaction is feasible in the
 temperature range considered.



Assumption:

(1) Ideal gas and ideal mixture

(2) Stack gases containing 0.05% mole equivalent of NO, 5% oxygen and 0.3% SO₂ at 1 atmosphere.

(3) Reaction #(1) at equilibrium at 600°K

Reference:

Data Sheets (1) and (5)

	$\text{NO} + 1/2 \text{O}_2 \rightleftharpoons \text{NO}_2$		at 600°K
Initial Concentration	0.05%	5%	-
	1 mole	100 moles	-
At Equilibrium	0.07 moles	99.54 moles	0.93 moles
Concentration Vol. %	0.0037%		0.0463%

	$\text{NO}_2 + \text{SO}_2 \rightleftharpoons \text{NO} + \text{SO}_3$		at 600°K
Initial Concentration	0.0463%	0.3%	0.0037%
	1 mole	6.5 moles	0.08 moles
At Equilibrium	0.001 moles	5.501 moles	1.08 moles
Concentration Mole %	0.013%	72.6%	14.2%
			13.2%
Vol. %	.005%	0.254%	.050%
			.046%

APPENDIX D

DERIVATION OF FIXED BED SORPTION MODEL

The following derivation of a fixed bed sorption model was taken from the USBM-Bruceton Report, RI-7021, dated July 1967, "Process Development in Removing Sulfur Dioxide From Hot Flue Gases; 3. Pilot Plant Study of the Alkalized Alumina System for SO₂ Removal". The sorption model shown is the one used for the design of the fixed bed process presented in the body of this report.

KINETIC STUDIES OF SO₂ ABSORPTION BY ALKALIZED ALUMINA¹⁹

Introduction

The purpose of this investigation was to develop a mathematical model which would accurately describe the removal of SO₂ from flue gas by alkalized alumina in fixed- and falling-bed reactors. Rate constants associated with the reaction were determined from data obtained in bench-scale tests. Using the model, these data were analyzed with the intention of gaining some insight into the factors which affect the reaction under various operating conditions. It is felt that such an understanding will be of great help in predicting and analyzing the behavior of large-scale systems operating under similar conditions.

Mathematical Analysis for Fixed-Bed Reactor

Nomenclature

- x = distance into column, ft
- t = time, hr
- y = SO₂ concentration in flue gas, by weight, dimensionless
- μ = SO₂ concentration on absorbent, by weight, dimensionless
- ρ_g = gas density, lb/ft³
- ρ_s = solid bulk density, lb/ft³
- F = void fraction of bed, dimensionless
- v = gas velocity, ft/hr
- A = cross sectional area of column, ft²
- G = ρ_g · v · F = flow rate of gas, lb/hr (ft²)
- S = feed rate of solids, lb/hr (ft²)
- K = reaction rate constant

A gaseous mixture containing SO₂ is passed continuously upward through a uniformly packed column of granular material. It is assumed that the concentration of SO₂ in the gas at the column inlet is constant for the time the column is in operation, and further that the gas flow rate (G) also remains constant. The sorbent material is initially assumed to be uncontaminated by SO₂, and finally we assume a constant temperature throughout the system. For such a situation, a material balance on SO₂ over a horizontal cross section of height Δx gives

$$\begin{array}{ccc} \text{(Rate of accumulation of SO}_2\text{)} & & \text{[(Input-Output)/unit time]} \\ \text{(on solid) (in void)} & & \\ \frac{\partial}{\partial t} [A(\Delta x)\rho_s\mu + A(\Delta x)\rho_g y F] & = & \frac{\partial}{\partial x} [\rho_g y A v F](\Delta x) \end{array} \quad (1)$$

¹⁹Prepared by M. J. Lempel, mathematician, Pittsburgh, Coal Research Center, Bureau of Mines, Pittsburgh, Pa.

This equation reduces to

$$\frac{\partial y}{\partial x} + \frac{1}{v} \frac{\partial y}{\partial t} = - \frac{\rho_s}{G} \frac{\partial \mu}{\partial t} \quad (2)$$

It can be shown that the term $\frac{1}{v} \frac{\partial y}{\partial t}$ may be neglected when the void volume of the fixed bed is negligible compared to the total volume of gas mixture passed through the bed. Therefore, equation 2 becomes

$$\frac{\partial y}{\partial x} = - \frac{\rho_s}{G} \frac{\partial \mu}{\partial t} \quad (3)$$

A second equation is obtained by postulating the rate at which SO_2 is absorbed by, or reacts with, the alkalized alumina. We assume that this rate is proportional to the product of concentration of SO_2 in the gas with the unreacted fraction of the solid. This is expressed by

$$\frac{\partial \mu}{\partial t} = K y \left(\frac{\mu_0 - \mu}{\mu_0} \right) \quad (4)$$

where μ_0 = total capacity of sorbent (lb/lb). The constant K appearing in equation 4 is not a true constant since it will depend upon such things as temperature, particle size, and porosity.

Equations 3 and 4 are to be solved for $y(x,t)$ and $\mu(x,t)$ subject to the boundary conditions,

$$y(0,t) = y_0 \quad \mu(x,0) = 0 \quad (5)$$

where y_0 = SO_2 concentration in gas at column inlet. Omitting the details, the solution is stated as follows:

$$y = \frac{y_0 e^{At}}{e^{At} + Bx - 1} \quad (6)$$

$$\mu = \mu_0 \left(1 - \frac{e^{Bx}}{e^{At} + Bx - 1} \right) \quad (7)$$

where $A = \frac{Ky_0}{\mu_0}$, $B = \frac{K\rho_s}{G}$.

APPENDIX E

DERIVATION OF DISPERSED PHASE SORPTION MODEL

The following derivation of a dispersed phase bed sorption model was contained in the Air Pollution Research Progress Report, Pittsburgh Coal Research Center, to Public Health Service for the Quarter Ended March 31, 1968 (i.e., USBM-Bruceton). The model shown was used in the present design of the dispersed phase process.

Q = quantity of solids contacted, lb
 r = sorption rate, hr⁻¹
 t = time, hr
 V = flue gas flow rate, SCFH
 v = volume of column, ft³
 w = SO₂ concentration on sorbent, weight fraction
 x = sulfur concentration on sorbent, weight fraction
 y = sulfur oxide concentration in flue gas, mole fraction
 Z = sorbent condition parameter
 ρ = average sorbent density, lb/ft³

Calculation of sorption rate

The average sorption rate ($\bar{r}$) observed within the column is expressed as the weight of SO₂ removed per weight of sorbent per hour.

$$\bar{r} = \frac{w}{t} \quad (1)$$

Sorbent weight is defined as the total weight of solid rather than that of sulfur-free alkalized alumina.

A material balance on SO₂ over the column height gives

$$\text{lb SO}_2 \text{ sorbed} = 0.178 (y_o - y_f)Vt \quad (2)$$

where the subscripts o and f indicate the column inlet and outlet, respectively, and t refers to gas contact time. Equation (2) neglects the change in gas volume due to sorption of SO₂ and assumes plug gas flow in a constant diameter tower. The quantity of solids contacted is given by

$$Q = \rho v \quad (3)$$

and if pressure loss due to wall friction and sorbent momentum is neglected

$$\rho = \frac{P}{0.1924h} \quad (4)$$

Comparison of measured solid densities and those calculated by equation (4) is shown in figure 1. Deviations are believed to be primarily due to the following factors:

- a. Experimental error in measurement of dilute solid density.
- b. Measurement of pressure loss over a portion of the column height, assuming pressure loss to be proportional to height, an assumption valid only for uniform solid density.

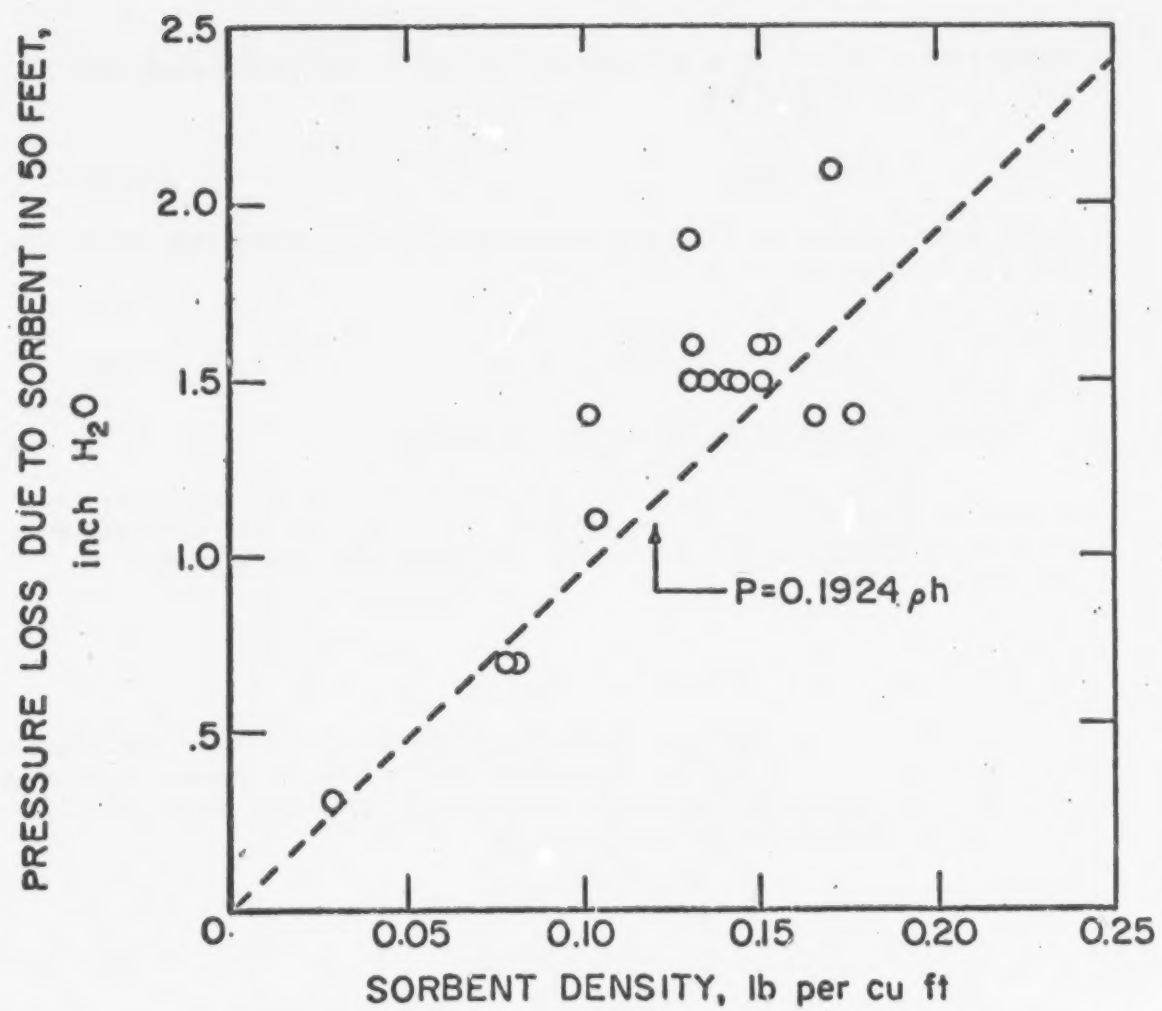


FIGURE E-75 - Measured and predicted sorber pressure loss.

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Substitution of (4) into (3) and use of the column cross-sectional area in place of $\frac{V}{h}$ gives

$$Q = 5.198pa. \quad (5)$$

Since w is defined as (2)/(5), insertion into (1) gives the expression for the average sorption rate:

$$\bar{r} = \frac{0.0342(y_o - y_f)V}{pa}. \quad (6)$$

Determination of Sorption Rate Constant

It is assumed that the sorption rate can be adequately represented as proportional to the product of two terms, one dependent only on sorbent condition and the second dependent only on flue gas concentration. Thus

$$r = \frac{dw}{dt} = Kf(Z, y). \quad (7)$$

If it is further assumed that sorbent is evenly distributed and contains a uniform quantity of sulfur throughout the column, Z becomes a constant dependent on operating conditions and sorbent quality. Equation (7) can thus be integrated and expressed as

$$\bar{r} = \frac{w}{t} = \frac{KZ}{t} \int_{t_o}^{t_f} f(y)dt = KZ\bar{y} \quad (8)$$

where $\bar{y}$ is the mean concentration in the flue gas, defined as

$$\bar{y} = \frac{1}{t} \int_{t_o}^{t_f} f(y)dt. \quad (9)$$

For plug gas flow at constant temperature and pressure, t may be replaced by h . If in addition $f(y)$ can be approximated by y^n such that

$$\frac{dy}{dh} = cy^n \quad (10)$$

equation (9) may be replaced by

$$\bar{y} = \frac{1}{h} \int_{h_o}^{h_f} [y_o^{n-1} + (n-1)ch]^{-\frac{1}{1-n}} dh. \quad (11)$$

Equation (10) predicts that a plot of $\log_{10} \frac{dy}{dh}$ versus $\log_{10} y$ will be a straight line of slope n . When averaged data of y versus h , presented in last quarter's report and reproduced here as figure 2, was graphically differentiated and tested in this manner, the result shown in figure 3 was obtained.

That a straight line was observed, indicates that the mean gas concentration predicted by equation (11) adequately describes sorber operation. The significance of the value found for n --approximately $2/3$ --is, however, not clear. Laboratory data indicate $n = 1$. Differences may be due to the inaccuracy inherent in the constant sorbent condition assumption or may be related to a change in reaction mechanism in the presence of nitrogen oxides. Further investigation is indicated.

Integration of (11) for $n = 2/3$ and insertion into (8) gives

$$\bar{r} = \frac{v}{t} = KZ \left[y_0^{-1/2} c y_0^{2/3} h + \frac{1}{9c^2} y_0^{1/3} h^2 - \frac{1}{108c^3} h^3 \right] \quad (12)$$

where c is evaluated using the integrated form of (10)

$$c = \frac{3}{h} \left[y_0^{1/3} - y_f^{1/3} \right]. \quad (13)$$

The sorbent condition parameter, Z , is expected to be a function of particle size and sulfur concentration distributions within the column. For the tests considered, however, this information is not available. As an approximation, Z is assumed to be a function of sulfur concentration alone. In addition the sorbent contacted is assumed to consist of particles having a linear loading distribution from the inlet to exit concentration. Thus

$$Z = f(\bar{x}) = f\left(\frac{x_0 + x_f}{2}\right). \quad (14)$$

If Z can be approximated by $\left(\frac{x_0 + x_f}{2}\right)^m$, equation (8) may be written

$$\log_{10} \frac{\bar{r}}{y} = \log_{10} K + m \log_{10} \left(\frac{x_0 + x_f}{2}\right) \quad (15)$$

and a plot of $\log_{10} \frac{\bar{r}}{y}$ versus $\log_{10} \left(\frac{x_0 + x_f}{2}\right)$ will be a straight line of slope m . The result of such a plot is shown in figure 4. The data, at least for test series E and F, may be approximated as a straight line of slope $= -1$ and $m = -1$ is assumed for all tests.

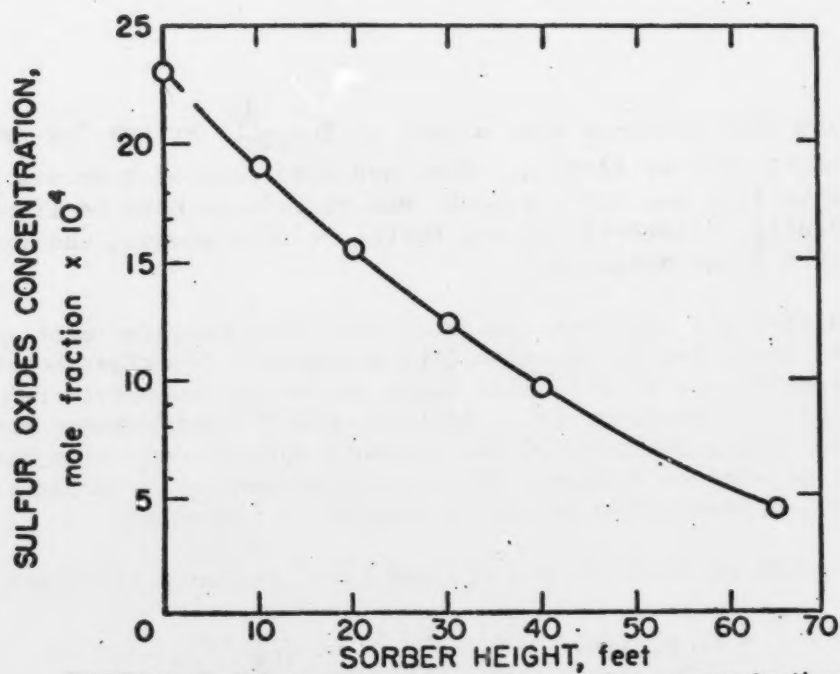


FIGURE E-76.-Variation in sulfur oxides concentration with sorber height.

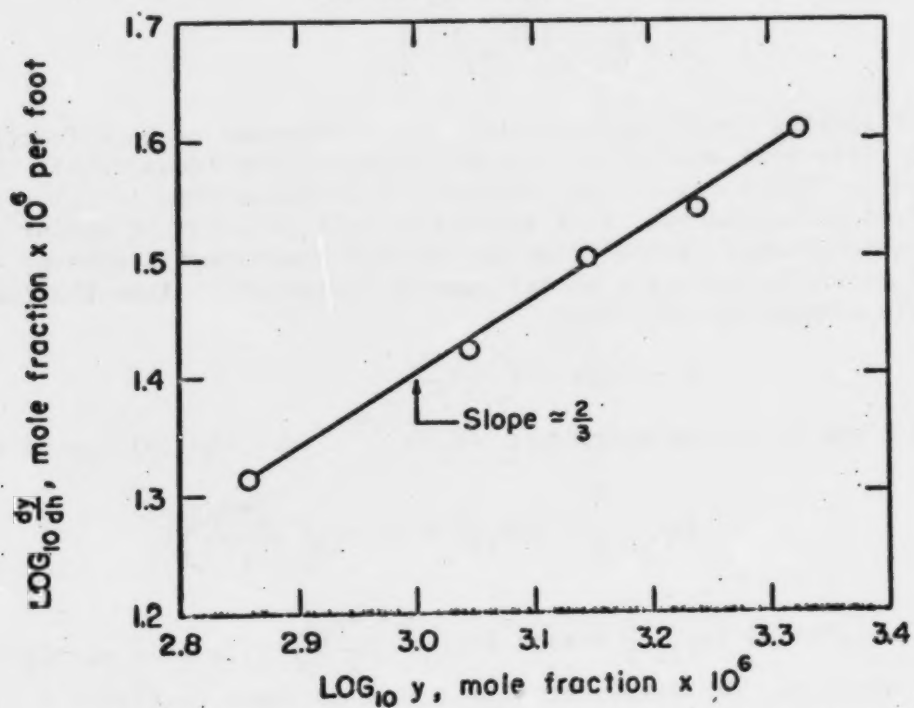


FIGURE E-77 -Test for predicting n in the equation

$$\frac{dy}{dh} = cy^n$$

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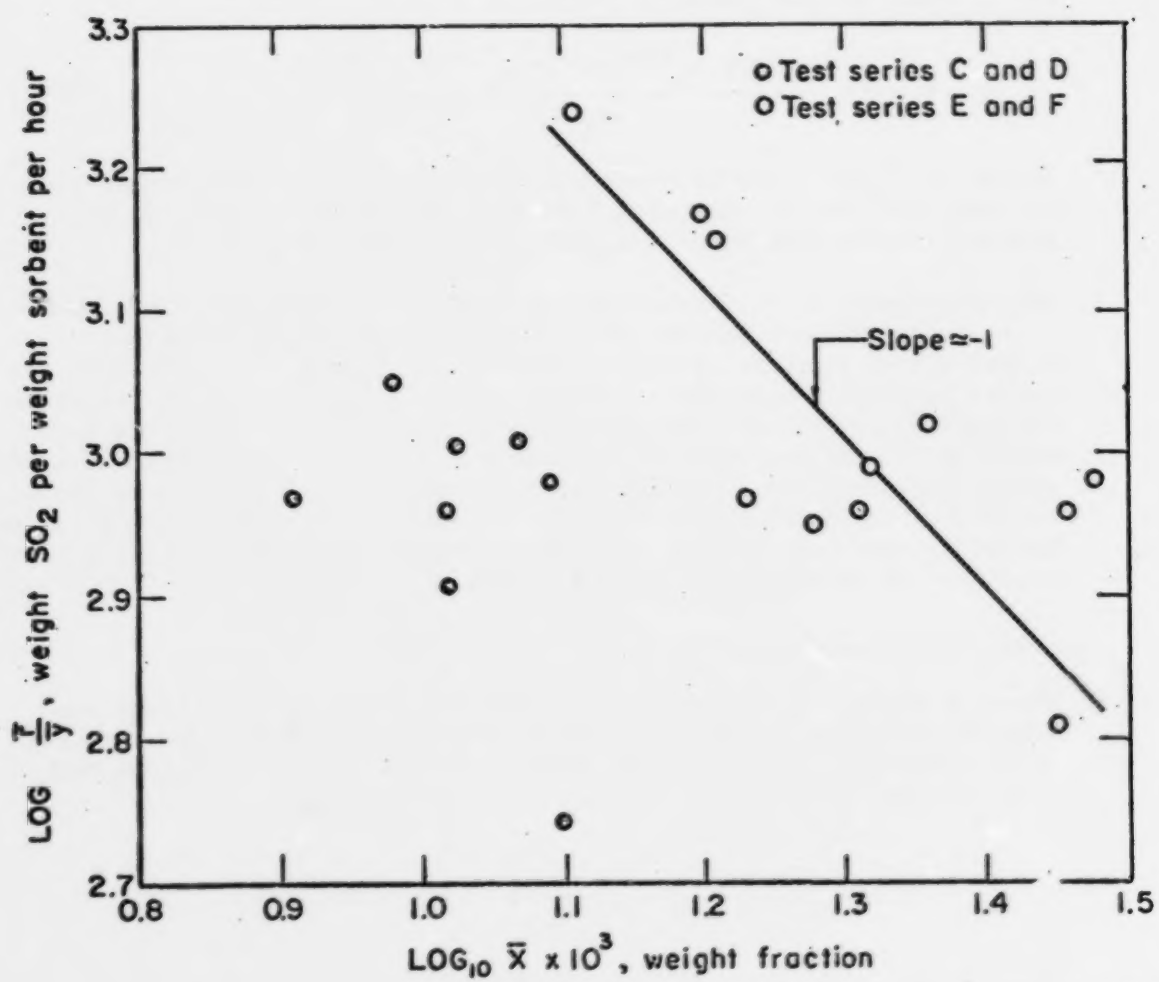


FIGURE E-78 - Test for predicting m in the equation $\frac{\bar{r}}{y} = k \left[\frac{x_0 + x_f}{2} \right]^m$

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The overall rate expression, then, is

$$\bar{r} = 2K \left[\frac{y_o - 1/2cy_o^{2/3}h + \frac{1}{9c^2}y_o^{1/3}h^2 - \frac{1}{108c^3}h^3}{x_o + x_f} \right]. \quad (16)$$

Values of $\bar{r}$ and K are tabulated in table 3 for the tests considered. For series C and D, K equaled 9.92 and for series E and F, 21.63. Standard deviations were 1.97 and 3.92, respectively.

The difference in calculated values of K is significant. The assumption of a linear sorbent loading distribution is extremely optimistic. Actual sulfur content of sorbent within the column is higher than predicted by this assumption. Results indicate that this ideal condition was more closely approximated in test series E and F where the total overhead stream was recycled than in C and D where a portion was removed after a single cycle. During the past quarter, the overall composition of sorbent in contact with the gas was determined over a wide range of operating conditions. The data should result in a more realistic expression for the sorbent condition term.

Prediction of Column Performance

The expressions developed should, over the range of conditions considered, predict column performance within about 20 percent. Sulfur oxides removal, pressure loss, flue gas flow rate, and initial and final sorbent loading are related by equation (16)

$$\bar{r} = 2K \left[\frac{y_o - 1/2cy_o^{2/3}h + \frac{1}{9c^2}y_o^{1/3}h^2 - \frac{1}{108c^3}h^3}{x_o + x_f} \right],$$

where $\bar{r}$ and c are defined by equations (6) and (13), respectively

$$\bar{r} = \frac{0.0342(y_o - y_f)V}{pa}$$

$$c = \frac{3}{h} \left[y_o^{1/3} - y_f^{1/3} \right].$$

Final sorbent loading may be replaced by sorbent feed rate if sorption is assumed to occur as sulfate, since from a SO_2 material balance

$$x_f = \frac{x_o L_f + 0.0890(y_o - y_f)V}{L_f + 0.2225(y_o - y_f)V} \quad (17)$$

TABLE - E-67 - Calculated values of sorption rate
and sorption rate constant

Test No.	r	K
C401	1.34	8.51
D104	1.66	12.20
D115	0.94	7.06
D120	1.38	7.49
D121	1.48	10.64
D122	1.36	11.87
D123	1.17	9.39
D124	1.25	12.21
E101	1.24	22.86
E102	1.16	18.60
E103	1.36	23.72
E104	1.15	20.20
E105	1.16	16.95
E106	1.05	15.73
F103	1.66	22.66
F104	1.60	23.61
F105	0.95	18.27
F106	1.28	26.03
F112	1.34	29.34

APPENDIX F

REGENERATION DATA

A summary is presented of the available data on regeneration of alkalized alumina. Sources of the data are indicated on the individual sheets. For a complete discussion of the data the original reports should be consulted.

TABLE F-68

RATE OF CONSUMPTION OF REDUCING GAS

SAMPLE NO.	REDUCING GAS	SULFUR, PERCENT BEFORE AFTER	RATE OF CONSUMPTION (CC/MIN)				
			600°C	620°C	640°C	660°C	680°C
26.	Pilot plant spent	H ₂ 2.5 0.7	--	1	6	--	--
28.	Pilot plant spent	H ₂ 2.5 0.6	--	1	7	10	--
32.	Pilot plant spent	H ₂ 2.5 0.9	--	2	6	9	19
33.	Pilot plant spent	H ₂ 2.5 1.4	--	1	7	11	20
34.	Pilot Plant spent	CO 2.5 2.0	3	7	11	--	--
38.	Pilot plant spent	CO 2.5 1.7	2	8	12	21	34
40.	Pilot plant spent	CO 2.5 1.8	4	9	13	22	35
46.	Bench-Scale spent	H ₂ 6.5 1.6	2	4	11	31	50
49.	Bench-Scale spent	CO 6.5 4.0	5	14	24	34	57
54.	Pilot plant fines	H ₂ 8.4 2.1	3	6	11	28	41
43.	Pilot plant fines	CO 8.4 7.0	--	9	16	25	42

Note: Initial charge was 4 grams.

Ref: USBM-Pittsburgh-Sec. II
3/31/68 Quarterly Report - Table I

APPENDIX F-69

REGENERATION OF GRACE NO. 1 SPENT SORBENT FROM PILOT PLANT MIXED PARTICLE SIZES, 5.3 PERCENT S*

Test No.	Reducing Gas	Temp. (°C)	Flow (cc/min.)	Space Vel. (hr ⁻¹)	Max. Consump. (cc/min.)	Total Consump. (cc/hr.)	Percent S		Reaction Time	% Wt. Loss
							Final	Removed		
82	H ₂	620	57	850	8	350	3.2	45.2	1 hr.	9.2
81	H ₂	640	55	825	17	810	1.8	71.4	1 hr.	15.4
83	H ₂	660	53	790	28	805	1.4	77.6	1 hr.	15.2
79	H ₂	660	52	780	39	730	1.4	77.1	45 min.	13.5
80	H ₂	660	52	780	29	755	1.7	72.4	1 hr.	13.9
86	CO	640	51	770	24	600	2.2	63.5	1 hr.	12.2
85	CO	660	91	1360	59	708	2.6	58.6	1 hr.	14.0
84	CO	680	93	1390	75	765	3.3	46.5	1 hr.	14.0
74	CO	660	61	920	--	---	3.3	45.5	80 min.	13.9
73	CO	640	62	930	28	720	2.1	65.4	70 min.	12.8
90	(H ₂ ⁺) (CO)	640	(38+) (19)	850	23	755	1.7	72.7	1 hr.	15.0
91	(H ₂ ⁺) (CO)	640	(19+) (40)	860	24	615	1.65	72.9	1 hr.	13.0
92	(H ₂ ⁺) (CO)	660	(26+) (28)	800	43	750	1.65	73.2	1 hr.	13.9

* USBM-Pittsburgh-Sec. II-6/30/68 Quarterly Report - Table 1.

Test Conditions: Differential Reactor - 4.25 gm charge
8 mm bed height
4 cm³ volume

TABLE F-70

HALF HOUR REGENERATION TESTS-ORIGINAL GRACE NO. 1 SORBENT*

(9.8 PERCENT SULFUR AND 1.0 PERCENT CARBON)

Test No.	Reducing Gas	Temp. (°C)	°F	Flow (cc/min)	Space Vel. (hr-1)	Max. Consump. (cc/min)	Total Consump. (cc/1/2 hr)	Percent S Final Removed	Percent Weight Loss	Percent Carbon
109	H ₂	620	1148	53.2	709	17.7	445	8.6	25.9	0.4
105	H ₂	640	1184	61.5	820	31.5	910	5.9	53.2	0.1
107	H ₂	660	1220	58.9	785	40.4	1100	3.4	74.5	0.1
108	H ₂	680	1256	73.3	977	61.5	1200	2.60	81.8	0.2
110**	H ₂	680	1256	37.0	1000	31.2	675	2.8	80.8	0.3
102	CO	620	1148	58.2	776	24.5	375	8.8	23.2	0.6
101	CO	640	1184	58.2	776	46.0	855	8.7	29.0	0.3
103	CO	660	1220	58.3	777	52.3	1135	9.2	30.2	0.2
104	CO	680	1256	72.7	969	66.1	1400	9.6	29.3	0.1

* USBM-Pittsburgh - Sec. II - 9/30/68 Quarterly Report - Table 1

** 2 gm Sample, Differential Reactor. All others contained 4.25 gms.

TABLE F-71

REGENERATION OF GRACE NO. 1 SORBENT-MODIFIED THIN BED TEST UNIT*

(SAMPLES LOADED IN DEEP FIXED-BED)**

TEMP. (°C)	REGENERATION TIME, (MINUTES)						Rate Constant, (Min ⁻¹)	
	0	4	8	16	30	60		120
	SULFUR, (PERCENT)							
Sample loaded to 8.8% S.								
600	8.66	8.72	8.50	8.46	8.45	8.75	9.00	.001
650	9.33	9.26	8.92	8.94	8.54	7.42	5.32	.005
680	8.10	8.87	8.05	7.23	5.57	2.70	1.22	.017
700	8.89	7.00	5.73	3.09	1.56	0.99	0.39	.059
700	8.80	6.36	4.49	2.37	1.29	0.85	0.23	.064
730	8.47	2.79	1.78	0.72	0.58	0.28	0.21	.195
Sample loaded to 5.87% S.								
600	5.96	5.77	5.45	5.92	4.97	5.23	5.28	.001
650	5.59	5.23	5.82	6.07	5.82	4.80	3.47	.004
680	5.86	5.46	5.34	3.56	3.07	1.73	0.62	.021
700	5.67	4.52	3.10	1.97	1.54	0.91	0.21	.044
730	5.70	2.24	0.87	0.61	0.33	0.25	0.14	.235
Sample loaded to 2.29% S.								
600	1.95	1.93	2.16	2.26	2.23	2.22	2.32	.001
650	2.33	2.05	1.92	2.03	1.92	0.87	0.62	.005
680	2.48	1.61	1.62	0.92	0.60	0.24	0.19	.058
700	2.18	0.91	0.73	0.42	0.29	0.15	0.12	-
730	2.40	0.54	0.44	0.25	0.13	0.16	0.13	-

* USBM-Albany - January 1969 Progress Report - Table 1

Test Conditions: 1.5" diameter sample holder; Simulated, Reformed Reducer Gas-50%N₂, 10%CO₂, 20%H₂, 5%H₂C; Gas Flow Rate - 0.12 ft³/min @ room temperature; Gas Velocity - 10 ft²/min; Space Velocity - 57,600 hr⁻¹ @ room temperature with the bed depth limited to a single pellet layer (1/8" deep).

** Pellet loads for the three samples are shown above the zero minute dry head analysis. The zero analyses show the spread in analyses from run to run, probably due to wide variation in load on the individual pellets.

TABLE F-72

REGENERATION OF SPENT ALKALIZED ALUMINA*

SPACE VELOCITY 1000 hr⁻¹; REACTION TIME = 1 hr

TEST NO.	SORBENT	REDUCING GASEX TEMP (°C)	REDUCING GAS FLOW (cc/min)	MAX. CONSUMP. REDUCING GAS (cc/min)	S		REMOVED (WT LOSS BASIS)	WEIGHT LOSS
					INITIAL	FINAL		
162	Kaiser PR-15	H ₂ 660	61	31.6	11.7	3.7	77.7	29.8
176	Kaiser DN-112-F		64.8	48.2	8.8	2.3	79.5	21.7
177	Kaiser DN-113-F		61.5	45	9.1	1.9	83.7	21.9
129	Kaiser (B) +		63.9	14.7	8.6	6.2	30.4	10.3
155	Kaiser DN-105+		62	10	10.4	9.6	13.6	6.0
157	Peter Spence +		63	8.3	10	10.2	4.7	6.6
149	USBM X-3-F		63.4	42.1	6.7	1.5	81.7	18.0
135	USBM 423-X-4E		65.5	51	6.2	2.5	66.3	15.7
138	Kaiser PR-15	H ₂ 680	64	51.1	11.7	2.3	86.7	32.5
169	Kaiser DN-112-F		64.5	53.5	8.8	2.1	81.3	21.7
170	Kaiser DN-113-F		60.5	51.3	9.1	1.7	85.3	21.5
154	Kaiser DN-105 +		65.8	16.9	10.4	8.5	25.3	8.5
156	Peter Spence +		61.2	15	10	8.9	19.4	9.5
160	Kaiser PR-15	H ₂ 640	60	15.7	11.7	9.1	33.3	14.2
136	USBM 423-X-4E	620	63	23.2	6.2	2.8	61	13.7
137	"	600	62.7	13	6.2	3.3	52.9	11.6
142	Kaiser PR-15	1:2 660	64.4	38.1	11.7	6.2	61.5	27.3
141	"	H ₂ :CO 1:2 660	65.6	34.3	11.7	5.5	66.3	28.3
140	"	H ₂ :CO 1:1 680	64.6	50	11.7	5.9	64.8	30.3
159	"	H ₂ :CO 1:1 640	62	23	11.7	8.2	42.8	18.4

* USBM-Pittsburgh - Sec. II - Dec. 21, 1968 Quarterly Report - Table I

Test Conditions: 1" diameter Vycor Reactor

4.25 gm charge

7-8 mm bed height

4 cm³ volume

+ Samples containing no iron. All other sorbents tabulated contained iron.

TABLE F-73

TWO-STEP REGENERATION OF SPENT ALKAL

SPACE VELOCITY $\approx 1000\text{hr}^{-1}$

NO.	SORBENT	REDUCING GAS	TEMPERATURE (°C)	REACTION TIME (Hrs)	REDUCING GAS FLOW (cc/min)
171	Kaiser DN-113-F	CO	680	1	59
173	"	CO then CO ₂	680 600	1 1/2	59.3
174	"	CO then CO ₂	680 300	1 1/2	59.3
172	"	CO then CO ₂ (3% H ₂ O)	680 600	1 1/2	60.5
175	"	CO then CO ₂ (3% H ₂ O)	680 300	1 1/2	59.7
178	"	CO	660	1	60
187	Kaiser DN-112-F	CO then CO ₂	680 600	1 1/2	60.2
186	"	CO then CO ₂	680 300	1 1/2	59.7
179	"	CO then CO ₂ (5% H ₂ O)	680 600	1 1/2	60
180	"	CO then CO ₂ (8% H ₂ O)	680 600	1 1/2	59.5
181	"	CO then CO ₂	680 100	1 1/2	59.9
166	Peter Spence +	CO then CO ₂ (3% H ₂ O)	660 300	1 1/2	60.5
167	"	CO then CO ₂ (3% H ₂ O)	660 600	1 1/2	60.5
165	"	CO then N ₂ (3% H ₂ O)	660 300	1 1/2	60
164	"	CO then N ₂ (3% H ₂ O)	660 600	1 1/2	59.5
150	USBM X-3-F	1:1-H ₂ :CO	640	1	62
151	"	1:1-H ₂ :CO then CO ₂	325- 640 220	1 1/2	63
148	"	CO	660	1	59
161	"	CO then CO ₂	660 300	1 1/2	60.5
153	"	CO then CO ₂	640 320- 130	1 1/2	60.3
143	USBM 423-X-4E	H ₂ then CO ₂	620 300- 210	1/2 1/2	61.8
144	"	H ₂ then CO ₂	620 325- 225	1 1/2	62.5
145	"	CO then CO ₂	620 325- 220	1 1/2	60
146	Kaiser PR-15	CO then CO ₂	620 320- 210	1 1/2	60.5
163	"	CO then N ₂ (3% H ₂ O)	660 600	1 1/2	61
168	Grace (1) B7M1	CO then CO ₂ (3% H ₂ O)	660 600	1 1/2	59

* USBM-Pittsburgh - Sec. II - Dec. 31, 1968 Quarterly Report - Table 2 Te

+ Samples containing no iron. All other sorbents tabulated contained iron.

TABLE F-73

-STEP REGENERATION OF SPENT ALKALIZED ALUMINA*

SPACE VELOCITY $\approx 1000\text{hr}^{-1}$

TEMPERATURE (°C)	REACTION TIME (Hrs)		REDUCING GAS FLOW (cc/min)	MAX. CONSUMP. REDUCING GAS (cc/min)		%S		%S REMOVED (WT. LOSS BASIS)	% WEIGHT LOSS
						INITIAL	FINAL		
680		1	59.7	52.4	9.1	7.1	36.8	19	
680	600	1 1/2	59.3	60	50.4	9.1	6.2	41.6	14.3
680	300	1 1/2	59.3	61.5	49.6	9.1	2.8	73.4	13.5
680	600	1 1/2	60.5	66.5	51.3	9.1	5.4	49.7	15.3
680	300	1 1/2	59.7	62.5	49	9.1	1.9	81.9	13.5
660		1	60	36.3	9.1	7.0	38	19.4	
680	600	1 1/2	60.2	59.5	49.6	8.8	5.8	43.4	14.1
680	300	1 1/2	59.7	60	45.5	8.8	2.9	71.6	13.8
680	600	1 1/2	60	58	49.5	8.8	5.5	46.7	14.7
680	600	1 1/2	59.5	60	49.5	8.8	5.4	47.3	14.2
680	100	1 1/2	59.9	60.8	48.2	8.8	8.2	24.7	19.1
660	300	1 1/2	60.5	61	15.7	10	9.5	12.3	7.7
660	600	1 1/2	60.5	60.5	14.3	10	9.3	14.4	8.0
660	300	1 1/2	60	59	14.4	10	9.9	8.2	7.2
660	600	1 1/2	59.5	61	16.1	10	9.5	12.9	8.3
640		1	62.8	29	6.7	2.5	69.3	17.7	
325- 640	220	1 1/2	63	59.5	29.7	6.7	1.1	86.3	16.3
660		1	59.5	34.7	6.7	5.4	32.5	16.3	
660	300	1 1/2	60.5	61.3	35.4	6.7	2.2	71.4	12.9
640	320- 130	1 1/2	60.3	54.7	22.5	6.7	2.3	69.9	12.3
620	300- 210	1/2 1/2	61.8	62.5	22.9	6.2	3.2	55.3	12.3
620	325- 225	1 1/2	62.5	59.2	19.5	6.2	2.3	68	13.6
620	325- 220	1 1/2	60	61	15.3	6.2	2.8	59.2	9.7
620	320- 210	1 1/2	60.5	61.2	26.6	11.7	9.6	27	11.8
660	600	1 1/2	61	59	43.1	11.7	9.1	41.8	25.2
660	600	1 1/2	59	61	29.8	2.3	0.7	71.5	10.4

Quarterly Report - Table 2 Test Conditions:

bents tabulated contained iron.

1" diameter Vycor Reactor
 4.25 gm charge
 7-8 mm. bed height
 $\approx 4\text{cm}^3$ volume

-F382-

TABLE F-74
REGENERATION OF SORBENTS USED FOR SO₂ REMOVAL
SPACE VELOCITY 1000hr⁻¹

TEST NO.	SORBENT	REDUCING GAS	TEMPERATURE (°C)	MAXIMUM RATE (cc/gm S/min)	OVERALL RATE (cc/gm S/min)	INITIAL %
182	BuM No. 466 ⁺ -17%Na	H ₂	660	27	16	8.2
183	BuM No. 467-22%Na	"	"	136	54	9.2
184	BuM No. 470-22%Na	"	"	135	52	8.8
185	BuM No. 472 ⁺ -22%Na	"	"	17	8	9.2
188	BuM No. 473-11%Na	"	"	163	47	6.5
189	BuM No. 474-17%Na	"	"	145	53	8.1
190	BuM No. 474-17%Na	H ₂ then CO ₂	660 300	143	53	8.1
191	BuM No. 474-17%Na	"	660 600	140	51	8.1
192	BuM No. 474-17%Na	"	660 100	144	53	8.1
199	BuM No. 473-11%Na	CO	680	187	48	6.5
198	BuM No. 473-11%Na	CO then CO ₂	680 300	180	48	6.5
200	BuM No. 473-11%Na	"	680 600	183	48	6.5
193	UOP-2	H ₂	680	266	52	4.9
194	UOP-2	H ₂	640	245	51	4.9
211	UOP-V-1	CO	680	180	50	6.7
212	UOP-V-1	CO then CO ₂	680 300	176	46	6.7
201	Kaiser PR-18-1	H ₂	680	134	56	9.3
202	Kaiser PR-18-1	H ₂	660	94	52	9.3
203	Kaiser PR-18-1	H ₂	640	63	40	9.3
206	Kaiser PR-18-1	CO	640	102	45	9.3
207	Kaiser PR-18-1	CO:H ₂ -5:1	640	102	50	9.3
208	Kaiser PR-18-1	CO:H ₂ -2:1	640	90	48	9.3

* USBM-Pittsburgh-Sec. II-March 31, 1969 Quarterly Report-Table 1.

Test Conditions: 4.25 gm charge with 7-8 mm bed height
60 cc/min reducing gas flow rate.
1.17 sec. superficial contact time @ 66
Reduction reaction using H₂, CO and the
1 hour, even though at the higher tempe
was completed before that time.

+ Samples containing no iron. All other sorbents tabulated contained iron.

R

TABLE F-74

REGENERATION OF SORBENTS USED FOR SO₂ REMOVAL*SPACE VELOCITY 1000hr⁻¹

ING	TEMPERATURE (°C)	MAXIMUM OVERALL RATE RATE (cc/gm S/min)		% SULFUR INITIAL FINAL		HARDNESS (LBS) REMOVED SPENT REGENERATED		
	660	27	16	8.2	7.0	20.7	14.0	15.0
	"	136	54	9.2	2.1	82.5	12.0	5.6
	"	135	52	8.8	2.8	74.8	14.8	7.9
	"	17	8	9.2	9.1	6.7	14.2	15.0
	"	163	47	6.5	2.1	73.2	13.6	10.8
	"	145	53	8.1	2.8	72.7	14.6	11.1
CO ₂	660 300	143	53	8.1	1.7	83.1	14.6	11.2
	660 600	140	51	8.1	1.9	81.3	14.6	11.0
	660 100	144	53	8.1	2.6	74.6	14.6	10.1
	680	187	48	6.5	4.7	39.2	13.6	11.3
CO ₂	680 300	180	48	6.5	2.2	70.1	13.6	12.7
	680 600	183	48	6.5	4.1	44.9	13.6	8.1
	680	266	52	4.9	2.2	61.3	10.3	9.4
	640	245	51	4.9	2.5	55.9	10.3	10.4
	680	180	50	6.7	5.1	36.8	2.4	4.2
CO ₂	680 300	176	46	6.7	1.4	81.8	2.4	4.7
	680	134	56	9.3	2.5	79.5	-	4.7
	660	94	52	9.3	2.5	79.8	-	3.5
	640	63	40	9.3	4.7	58.6	-	3.8
	640	102	45	9.3	5.5	52.5	-	4.9
:1	640	102	50	9.3	4.1	65.6	-	3.6
:1	640	90	48	9.3	4.1	65.5	-	3.6

1969 Quarterly Report-Table 1.

4.25 gm charge with 7-8 mm bed height

60 cc/min reducing gas flow rate.

1.17 sec. superficial contact time @ 660°C

Reduction reaction using H₂, CO and these mixtures was usually terminated after 1 hour, even though at the higher temperatures consumption of the reducing gas was completed before that time.

other sorbents tabulated contained iron.

B

TABLE F-75

REGENERATION OF GRACE 1 AND GRACE 2 SATURATED WITH SO₂, SPAC

TEST NO.	SAMPLE PREP.	REGENERATION GAS	TEMP. (°C)	MAXIMUM RATE (cc/gm S/min)	OVERALL RATE (cc/gm S/min)	SULFUR INITIAL
209	Grace 1	CO then CO ₂	680 Room 680 → Temp.	101	53	12.5
210	Grace 2	CO then CO ₂	680 Room 680 → Temp.	107	53	11.9
217	Grace 1	H ₂	700	106	54	12.5
218	Grace 2	H ₂	700	112	54	11.9
227	Grace 1	H ₂	680	102	53	12.5
220	Grace 2	H ₂	680	99	53	11.9
225	Grace 1	H ₂	640 (2 hrs.)	44	25	12.5
224	Grace 2	H ₂	640 (2 hrs.)	56	24	11.9
221	Grace 2	1:1, H ₂ :CO then CO ₂ (5% H ₂ O)	680 250 (0.5 hr.)	104	54	11.9
222	Grace 2	1:1, H ₂ :CO then CO ₂ (5% H ₂ O)	680 250 (1 hr.)	110	54	11.9

* USBM-Pittsburgh-Sec. II-March 31, 1969 Quarterly Report - Table 3.

Test Conditions: 4.25 gm charge with 7-8 mm bed height
 60cc/min reducing gas flow rate
 1.17 sec. superficial contact time @ 660°C
 Reduction reaction using H₂, CO, and their mixtures was usually terminated after 1 hr., even though at the higher temperatures consumption of the reducing gas was completed before that time.

A

TABLE F-75

GRACE 1 AND GRACE 2 SATURATED WITH SO₂, SPACE VELOCITY ~1000 hr⁻¹*

MAXIMUM RATE (cc/gm S/min)	OVERALL RATE (cc/gm S/min)	SULFUR, PERCENT			HARDNESS, (LBS)	
		INITIAL	FINAL	REMOVED	SPENT	REGENERATED
101	53	12.5	7.2	52.2	12.4	4.4
107	53	11.9	6.8	52.2	6.9	3.0
106	54	12.5	2.9	84.4	12.4	3.0
112	54	11.9	3.0	82.6	6.9	0.8
102	53	12.5	3.2	82.7	12.4	2.4
99	53	11.9	3.9	77.4	6.9	1.5
s.) 44	25	12.5	3.4	81.6	12.4	1.8
s.) 56	24	11.9	3.7	78.5	6.9	0.9
104	54	11.9	2.8	82.4	6.9	2.1
hr.)						
110	54	11.9	1.2	92.4	6.9	1.8
t.)						

Quarterly Report - Table 3.

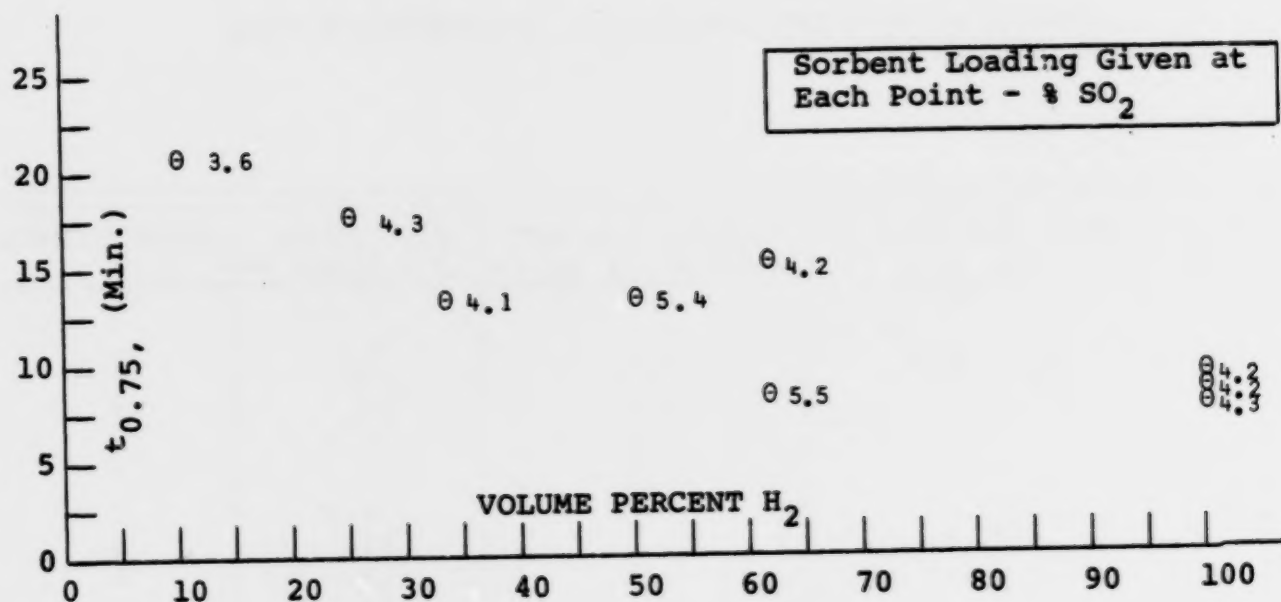
7-8 mm bed height
s flow rate

l contact time @ 660°C

using H₂, CO, and their mixtures was usually
r., even though at the higher temperatures
educing gas was completed before that time.

B

TABLE F-76

EFFECT OF H₂ PARTIAL PRESSURE ON REGENERATION TIME

RUN	TEMP. (°C)	REGENERATION GAS COMPOSITION (VOL. %)	INITIAL SORBENT LOADING (% SO ₂)*	REGENERATION TIME (75% COMPLETION)**
R-3	650	H ₂ - 100	4.2	7.7
R-5	"	" - "	4.3	7.2
R-6	"	" - "	4.2	8.9
R-7	"	H ₂ -N ₂ - 50/50	5.4	13.
R-8	"	" - 12.2/87.8	3.6	20.8
R-9	"	" - 26/74	4.3	17
R-10	"	" - 33.1/66.9	4.1	13
R-13	"	" - 61.2/38.8	5.5	8.5
R-21	"	" - 61.2/38.8	4.2	15

Ref: AVCO FINAL REPORT
TABLE 8 - p. 106
NOVEMBER 1, 1967

* Sulfur free basis.

** 75% of weight gained during sorption.

TABLE F-77

EFFECT OF SORBENT LOADING ON REGENERATION TIME

RUN	TEMP (°C)	REG. GAS COMP. (VOL %)	INITIAL SORBENT LOADING (% SO ₂) *	REG. TIME (75% COMP. ***)	GRAPH SYMBOL
P-5B	650	H ₂ - 100	2.8	3.	X
P-6A	"	"	9.4	17.	"
R-3	"	"	4.2	7.7	"
R-5	"	"	4.3	7.2	"
R-6	"	"	4.2	8.9	"
R-56	"	"	37. **	95.	Δ
R-71	"	"	7.2 **	11.	Δ
R-72	"	"	8.6 **	14.5	Δ
R-57	700	H ₂ - 100	33. **	22.	◇
R-58	"	"	41. **	31.	"
R-62	"	"	31. **	8.	"
R-63	"	"	28.5 **	9.	"
R-13	650	H ₂ -N ₂ -61.2/38.8	5.5	8.5	O
R-16	"	"	2.4	4.	"
R-17	"	"	2.2	4.9	"
R-19	"	"	6.1	13.	"
R-20	"	"	2.5	5.3	"
R-21	"	"	4.2	15.	"

*Sulfur free basis.

**Sorption with wet flue gas

***75% of weight gained during sorption

 Ref: AVCO FINAL REPORT
 TABLE 8 - p. 106
 NOVEMBER 1, 1967

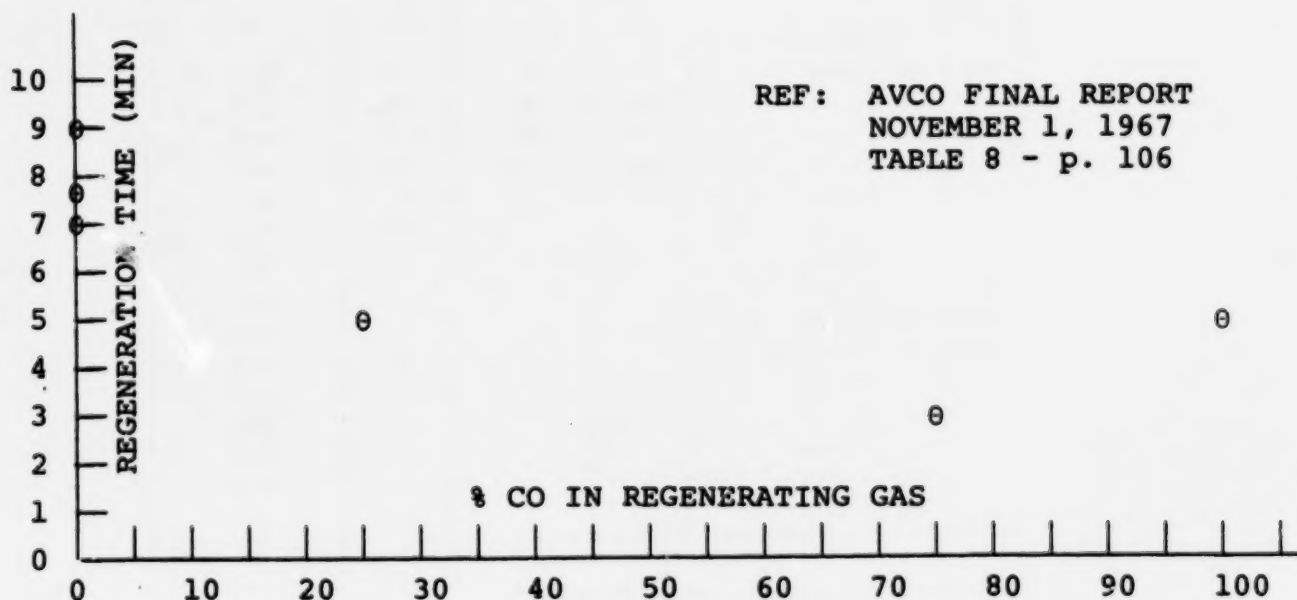
TABLE F-78

EFFECT OF CARBON MONOXIDE ON REGENERATION TIME

RUN	TEMP (°C)	REG. GAS. COMP. (VOL %)	INITIAL SORBENT LOADING (% SO ₂)*	REG. TIME (75% COMP.)
R-24	650	CO - 100	4.9	5.2**
R-27	"	H ₂ -CO; 75/25	4.1	5. **
R-28	"	H ₂ -CO; 25.5/74.5	4.7	3.2**
R-3	"	H ₂ -100	4.2	7.7
R-5	"	"	4.3	7.2
R-6	"	"	4.2	8.9

*Sulfur free basis

**In the presence of CO, regeneration time is defined as the time required to remove 75% of the sorbate that can be removed before reaching equilibrium as opposed to 75% of the weight gained during sorption.



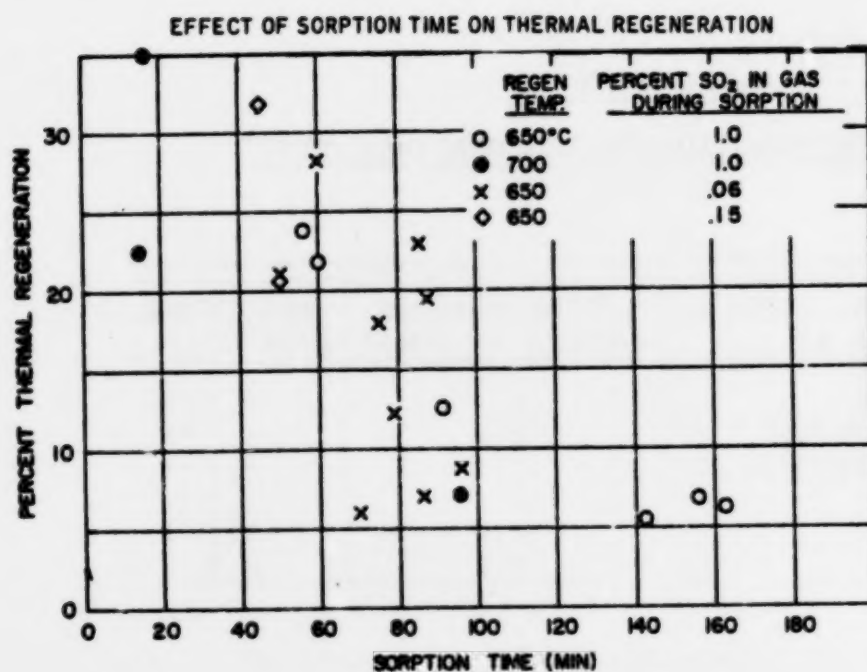


TABLE F-79

REF: AVCO FINAL REPORT
PP. 104-106
NOVEMBER 1, 1967

REGENERATION DATA FOR SO₂ SORPTION (T_{sorption} = 300° C)

Run	T(°C)	Regeneration gas Composition (volume percent)	Initial Loading (mg/mg)	Regeneration Time (min)	Sorption time (min)	Weight loss upon heating in H ₂ , percent of gain in sorption
R-56	650	H ₂ -100	.37	95	95	7.0
R-57	700	H ₂ -100	.33	22	91	12.6
R-58	700	H ₂ -100	.41	31	152	6.2
R-59	700	H ₂ -69.7, H ₂ S-7.2 H ₂ O-22.8	.367		155	6.8
R-60	700	H ₂ S + H ₂ - H ₂ S meter broken	.372		142	5.5
R-62	700	H ₂ -100	.31	8	60	21.8
R-63	700	H ₂ -100	.285	9	56	23.8
R-71	650	H ₂ -100	.072	11	14	22.6
R-72	650	H ₂ -100	.086	14.5	16	34.8
ISR-1	650	H ₂ -100			45	31.8
ISR-2	650	H ₂ -100			50	20.6
ISR-3	650	H ₂ -100			85	22.9
ISR-4	650	H ₂ -100			87	19.4
ISR-5	650	H ₂ -100			79	12.2
ISR-6	650	H ₂ -100			60	28.2
ISR-7	650	H ₂ -100			70	5.9
ISR-1 ¹	650	H ₂ -100			50	21.0
ISR-2 ¹	650	H ₂ -100			86	6.9
ISR-3 ¹	650	H ₂ -100			75	18.0
ISR-5 ¹	650	H ₂ -100			95.2	8.7

*computed as $.8 \times \frac{\text{weight gain during sorption}}{\text{weight of sorbent}}$

Note: CO₂ present in simulated flue gas for R-58 through R-72 absent for R-56 through R-72

TABLE F-80
EFFECT OF TEMPERATURE ON REGENERATION TIME

RUN	TEMP. (°C)	REG. GAS COMP. (VOL %)	INITIAL SORBENT LOADING (% SO ₂)*	SORPTION CONDITIONS	REG. TIME (75% COMP.)**
R-23	550	H ₂ - 100	4.3	Dry Flue Gas	36.0
R-3	650	"	4.2	" "	7.7
R-5	650	"	4.3	" "	7.2
R-56	650	"	37.0	Wet Flue Gas	95.0
R-57	700	"	33.0	" "	22.0
R-58	700	"	41.0	" "	31.0

- 3389 -

*Sulfur free basis

**75% of weight gained during sorption

Ref: AVCO FINAL REPORT
TABLE 8, P. 106
NOVEMBER 1, 1967

TABLE F-81

TWO-STEP REGENERATION SUMMARY-GRACE NO. 2 SORBENT⁺

REDUCTION				REGENERATION				
Run #	Wt % S Absorbed	Time (Min)	Temperature °F	CO Flow Rate VHSV	Time (Min)	Temperature (°F)	Flow Rate VHSV	Final Analysis %H ₂ O (Wt %)
5650-243	5.07	20	1270	2625	75	500	1211	20
5650-244	4.86	75	1200	2625	40	340	750	50
5650-245*	4.83	75	1200	1500	50	340	750	50
5650-246	4.92	45	1200	1500	20	340	750	25
5650-247	4.92	60	1250	1500	50	500	750	25
5650-248	5.18	60	1200	2625	40	500	750	13

* Sample to be rerun to confirm data.

⁺ W. R. Grace & Co.- Jan. 1969 Monthly Report - Table III

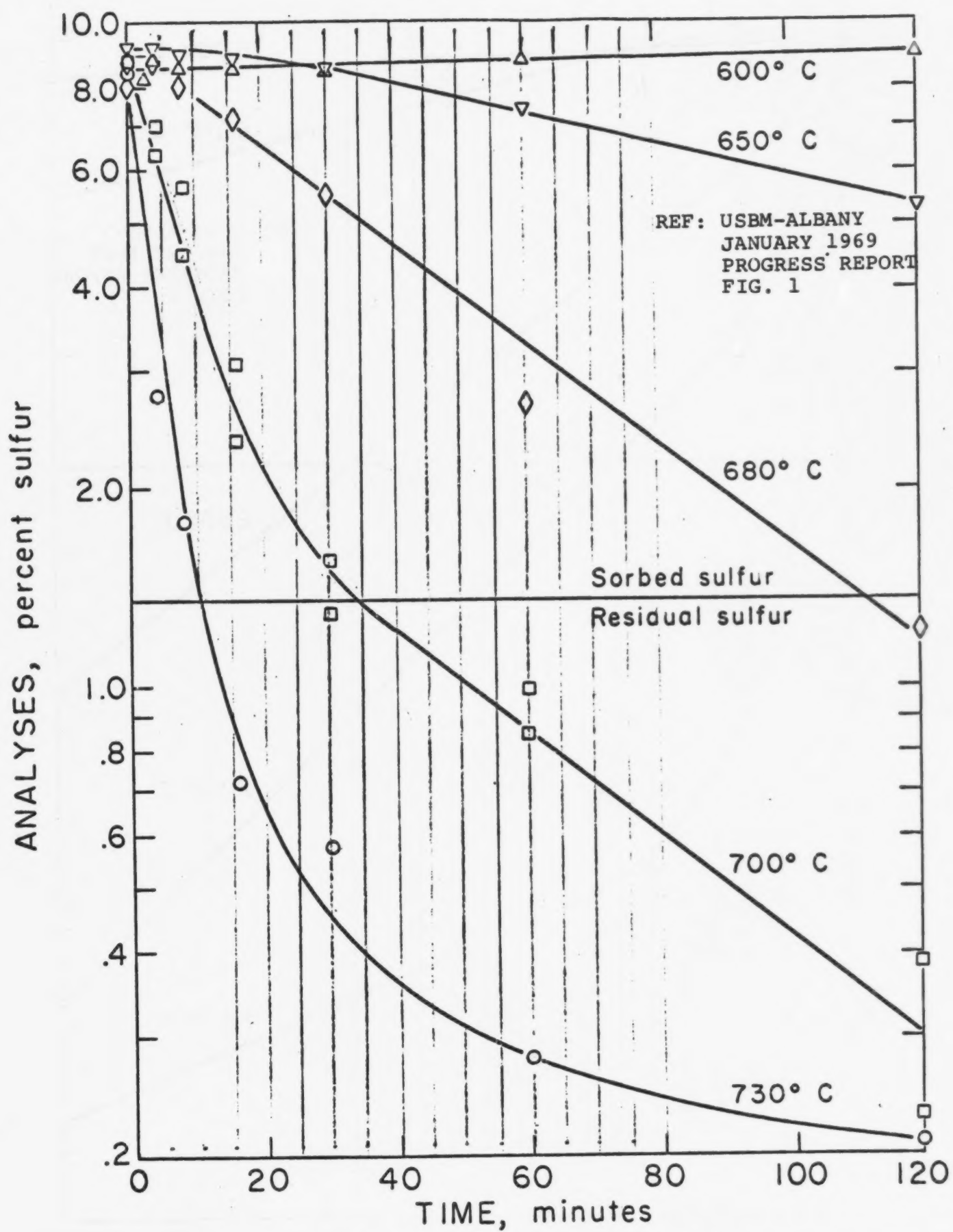


FIGURE F-79.-Effect of Time and Temperature on Sulfur Removed (Grace No. 1-8.5 pct S).

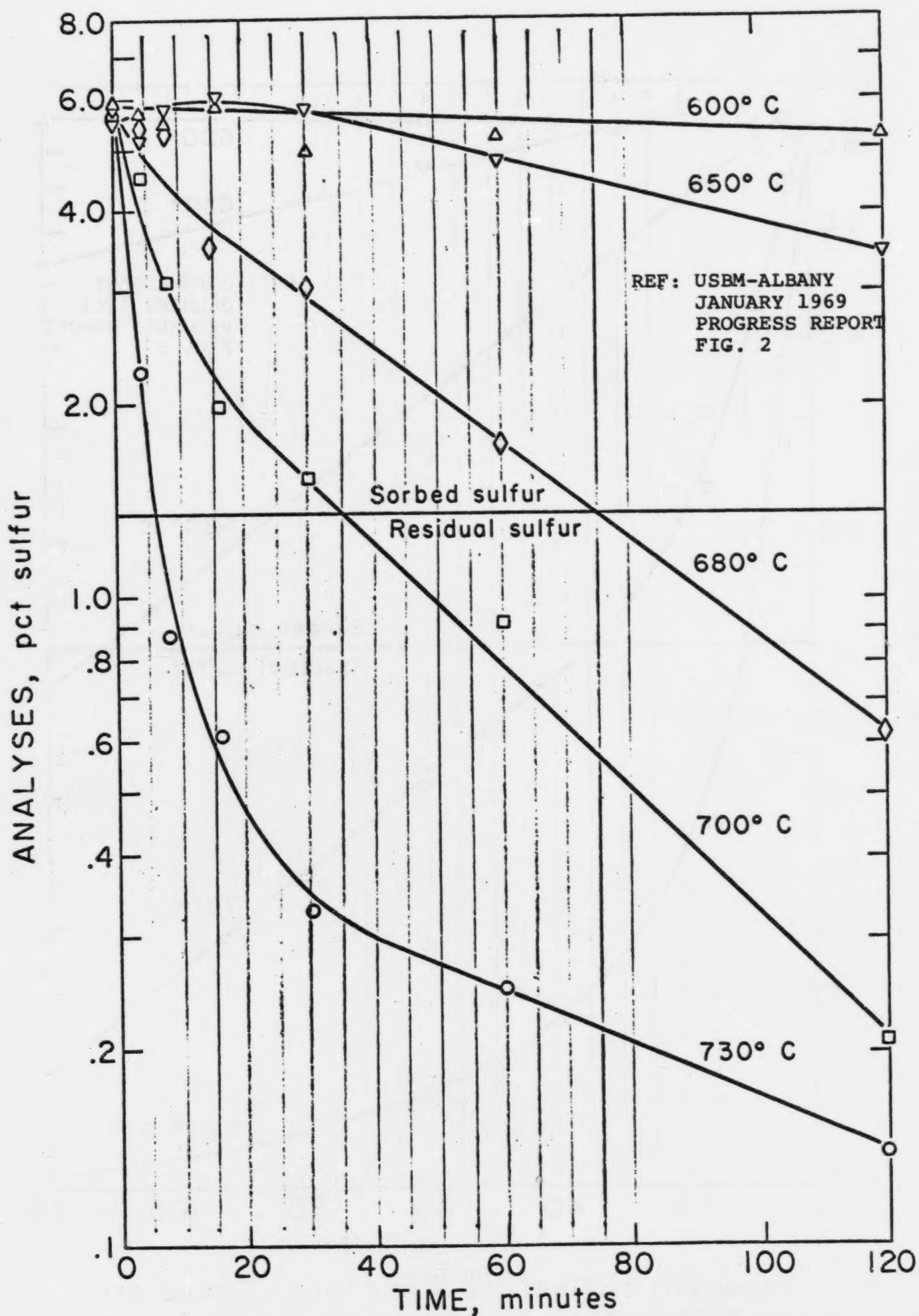


FIGURE F-80 -Effect of Time and Temperature
on Sulfur Removed (Grace No. 1-5.5 pct S).

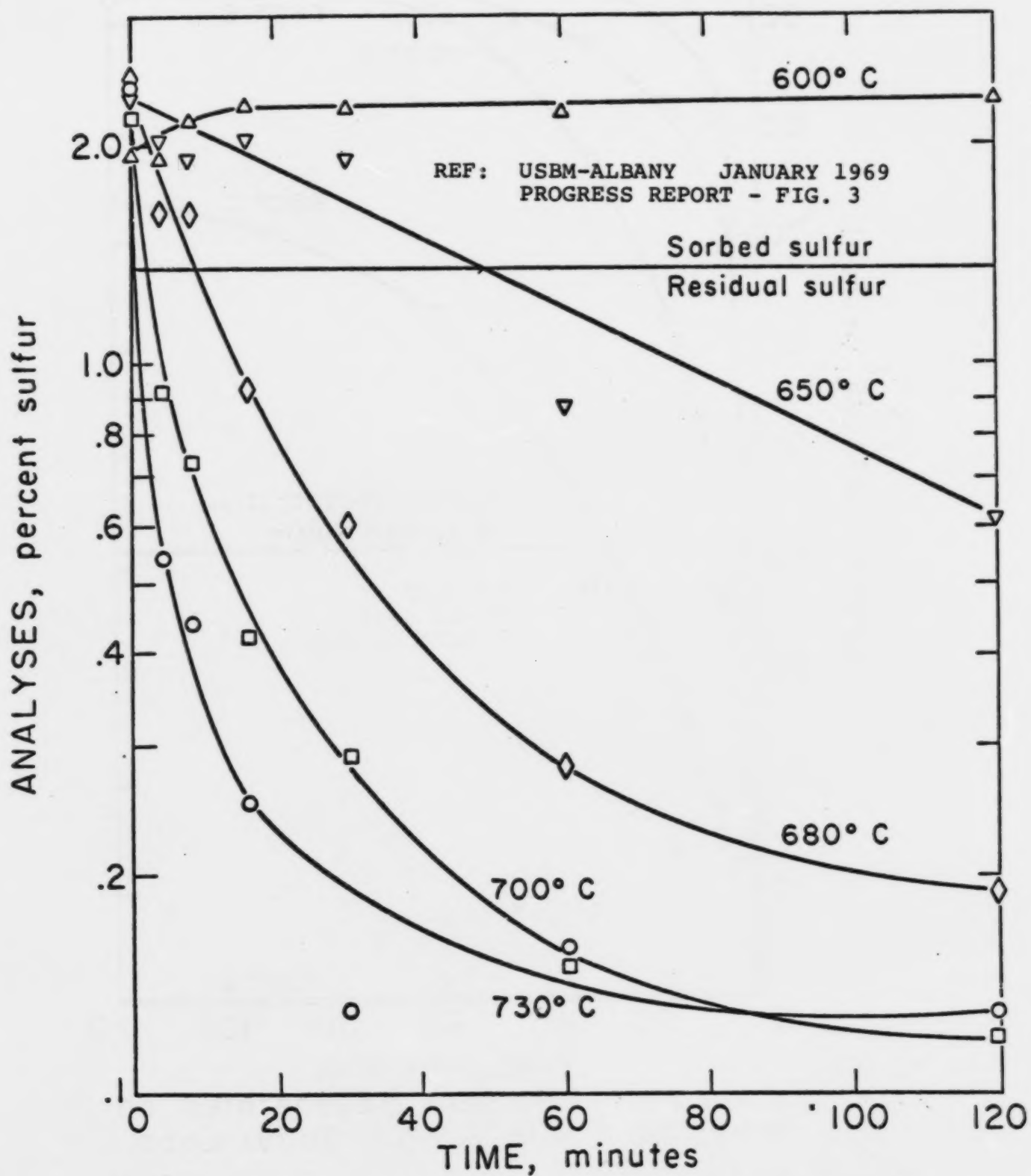


FIGURE F-81 -Effect of Time and Temperature on Sulfur Removed (Grace No. 1-2.3 pct S).

69-31

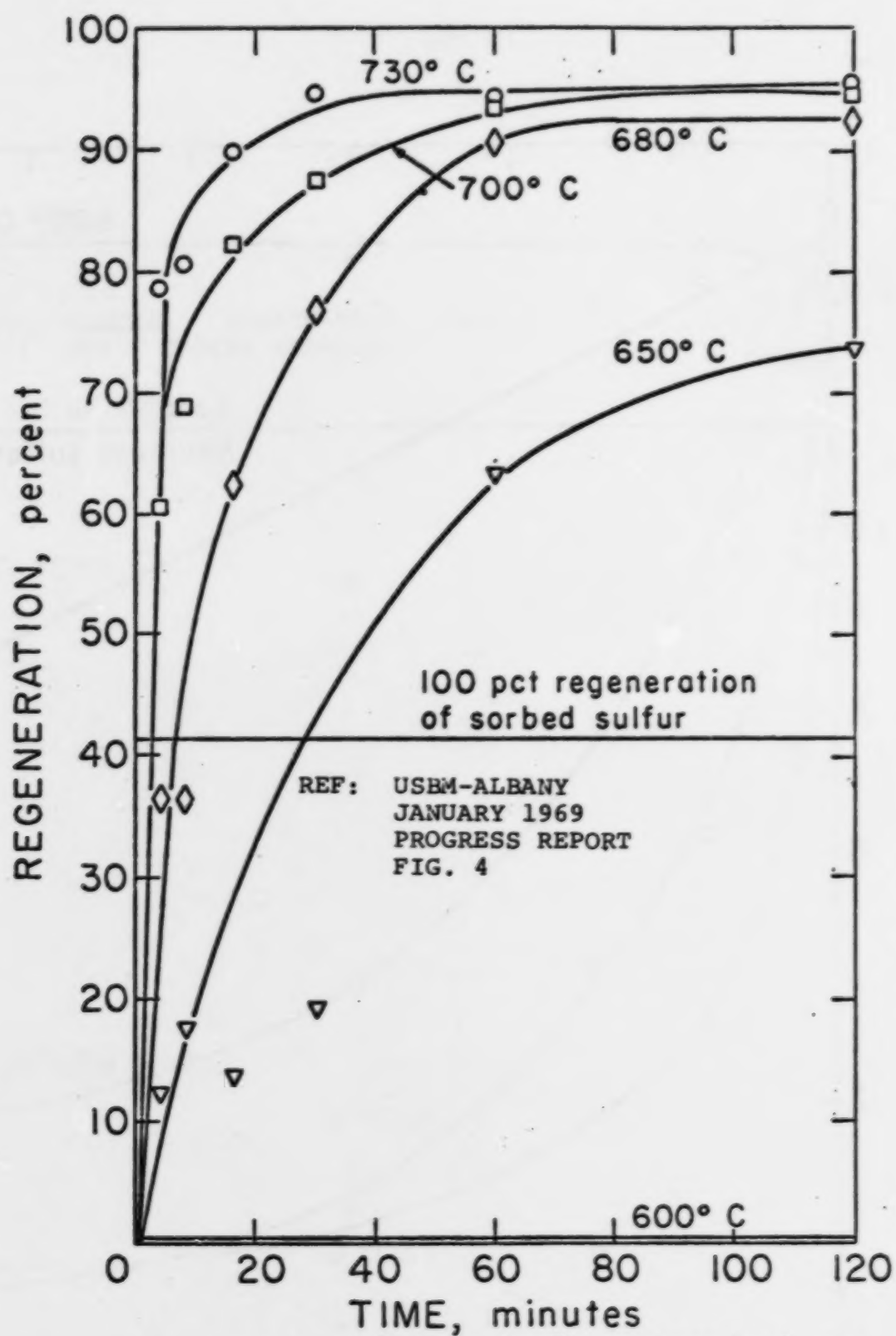


FIGURE F-82 -Percent Regenerated on Grace No. 1 with 2.3 pct Sulfur Load.

69-32

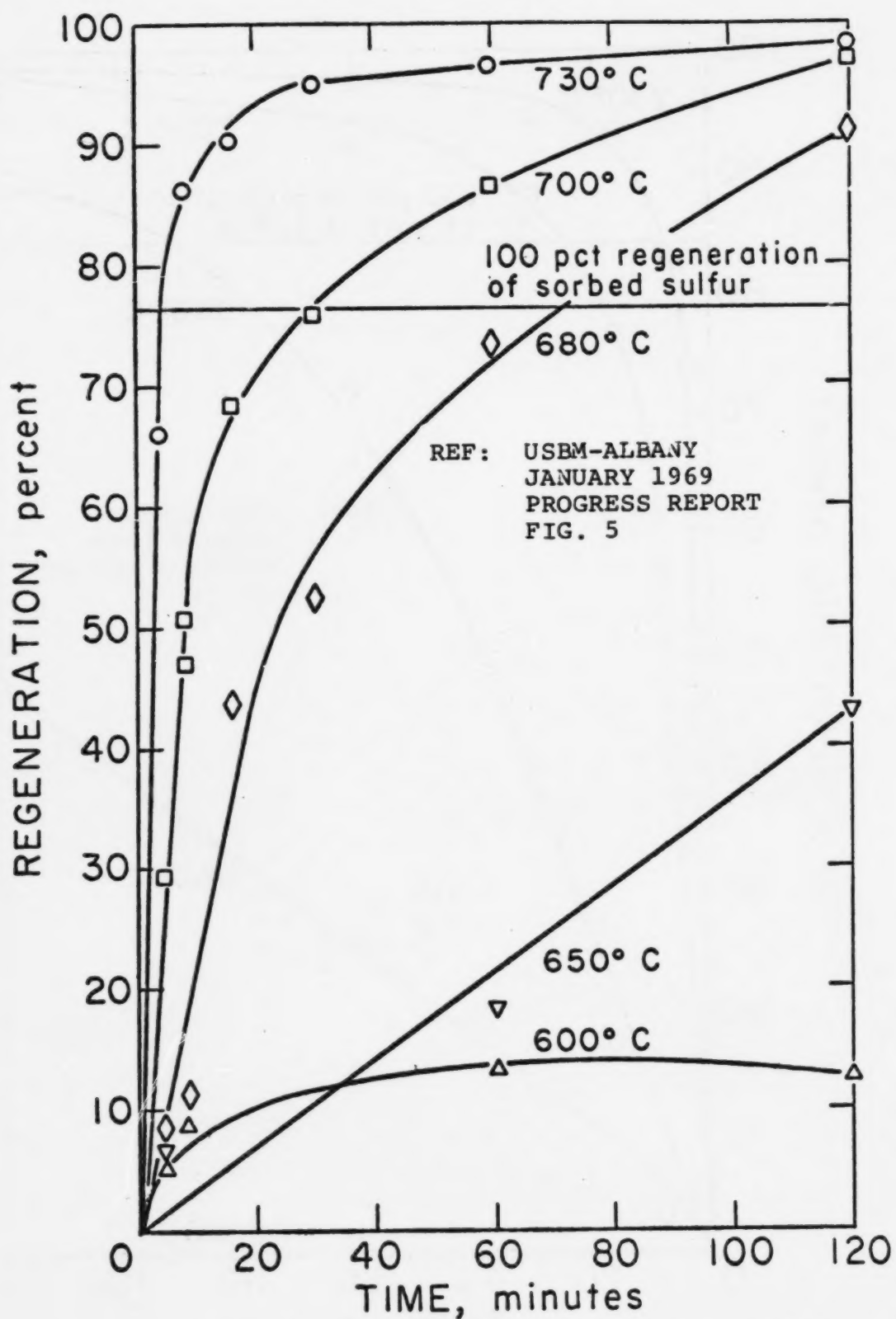


FIGURE F-83 - Percent Regenerated on Grace No. 1 with 5.5 pct Sulfur Load.

69-33

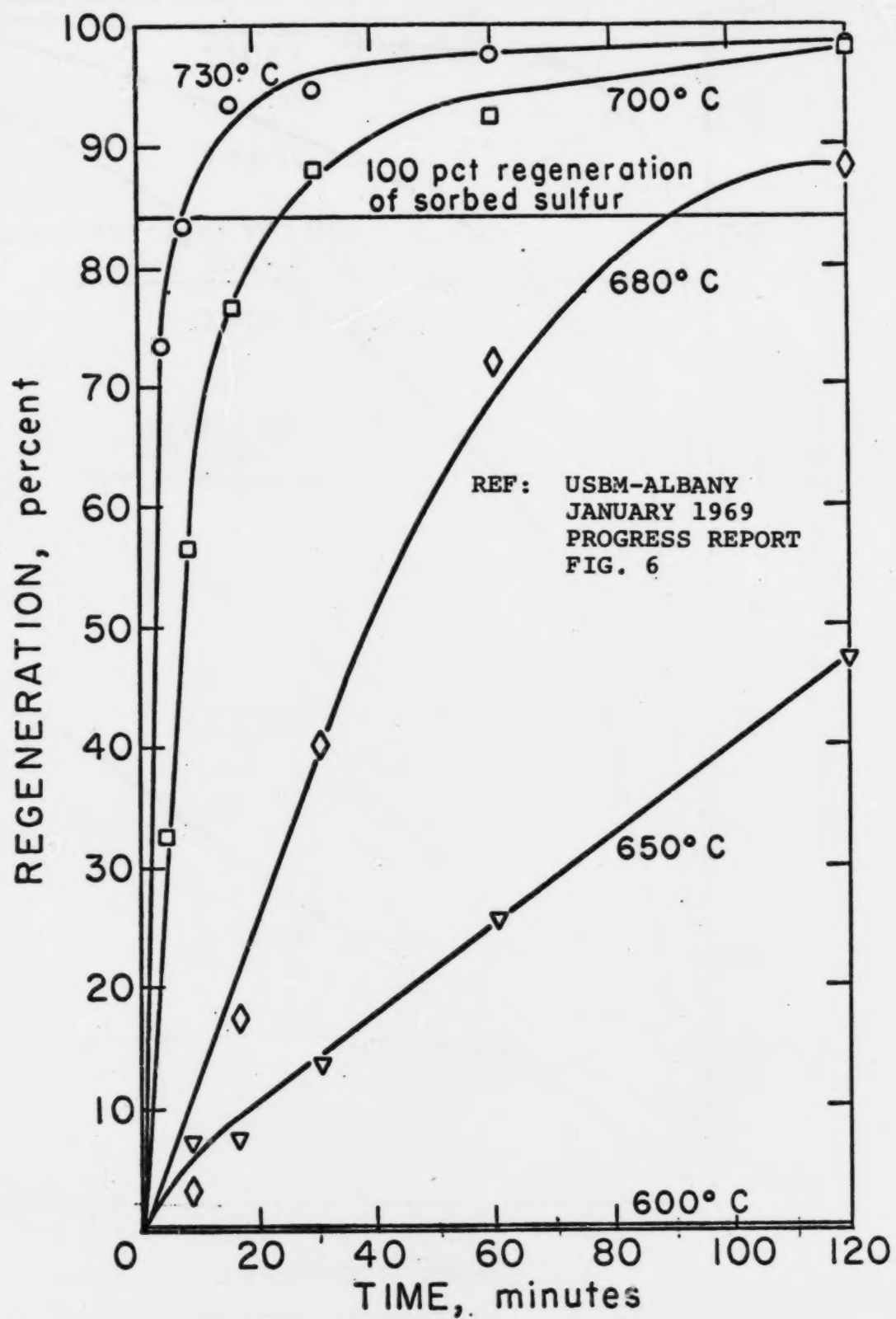


FIGURE F-84 - Percent Regenerated on Grace No. 1 with 8.5 pct Sulfur Load.

69-34

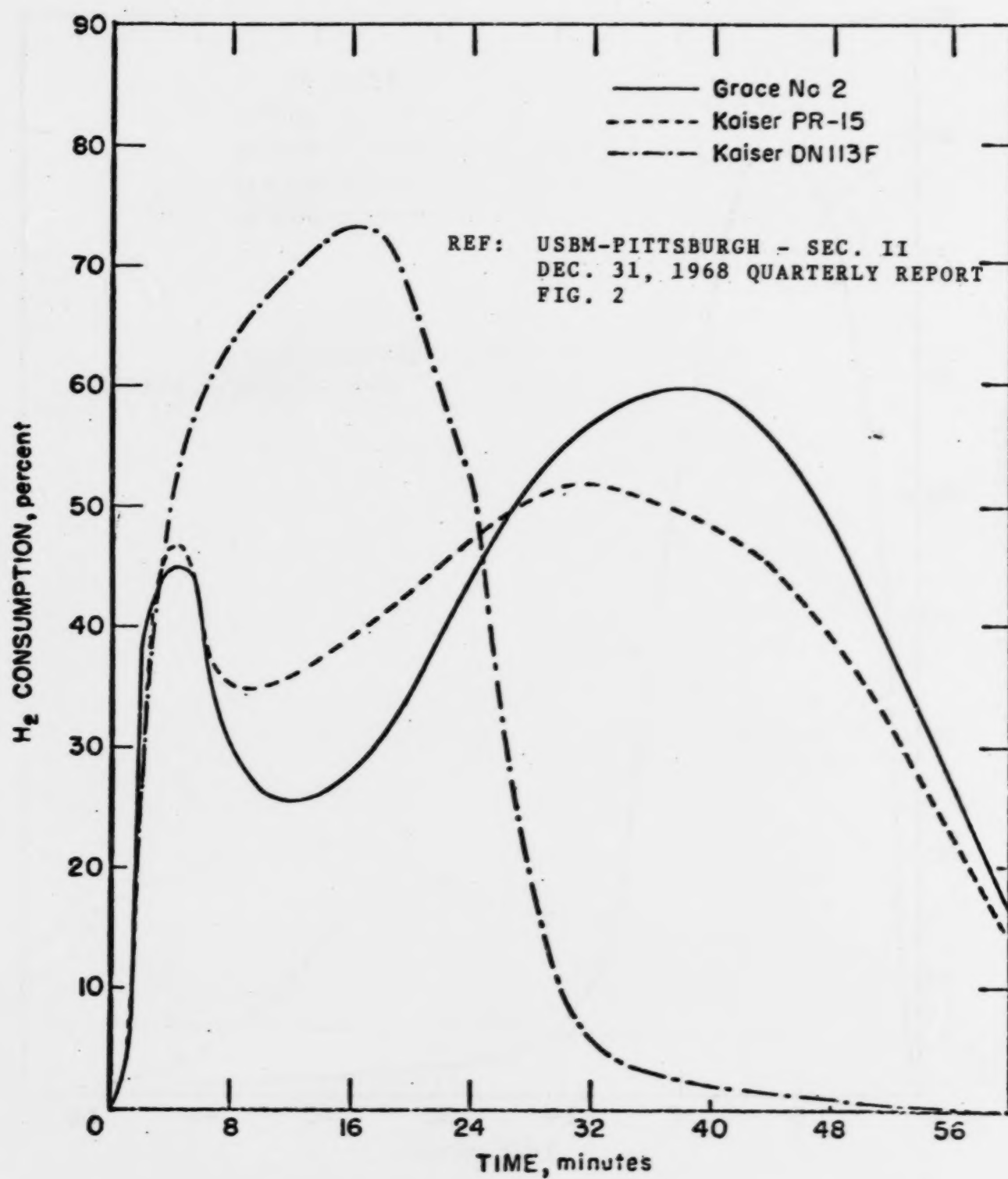


FIGURE F-85 H_2 utilization at $660^\circ C$ and 1000 hr^{-1} space velocity for commercial sorbents containing iron.

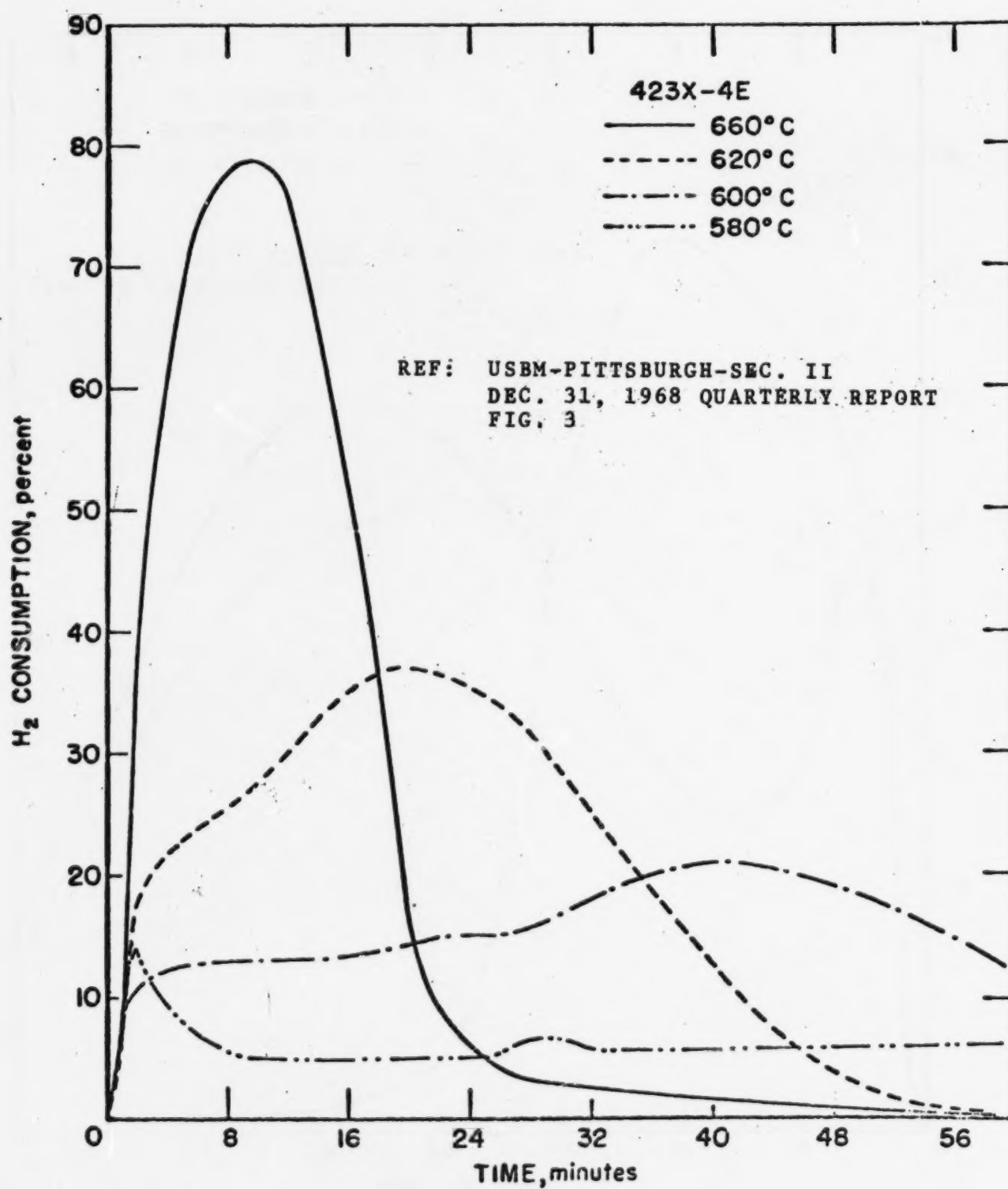


FIGURE F-86 H₂ utilization at 1000 hr⁻¹ space velocity of Bureau's 423-X-4E at four different reaction temperatures.

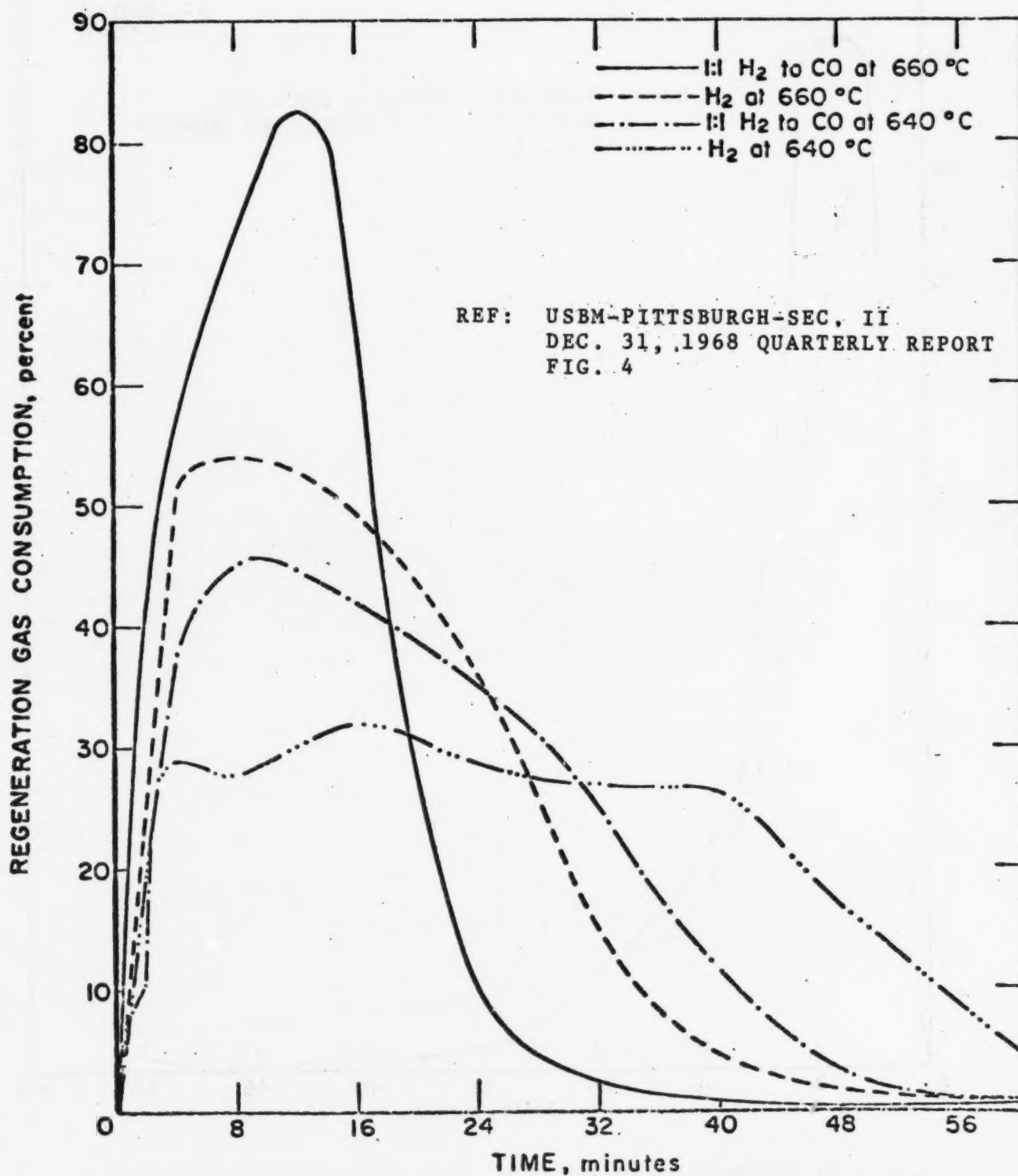


FIGURE F-87 Utilization of Regeneration Gas for Grace (1) at 660° and 640°C and 1000 hr⁻¹ space velocity.

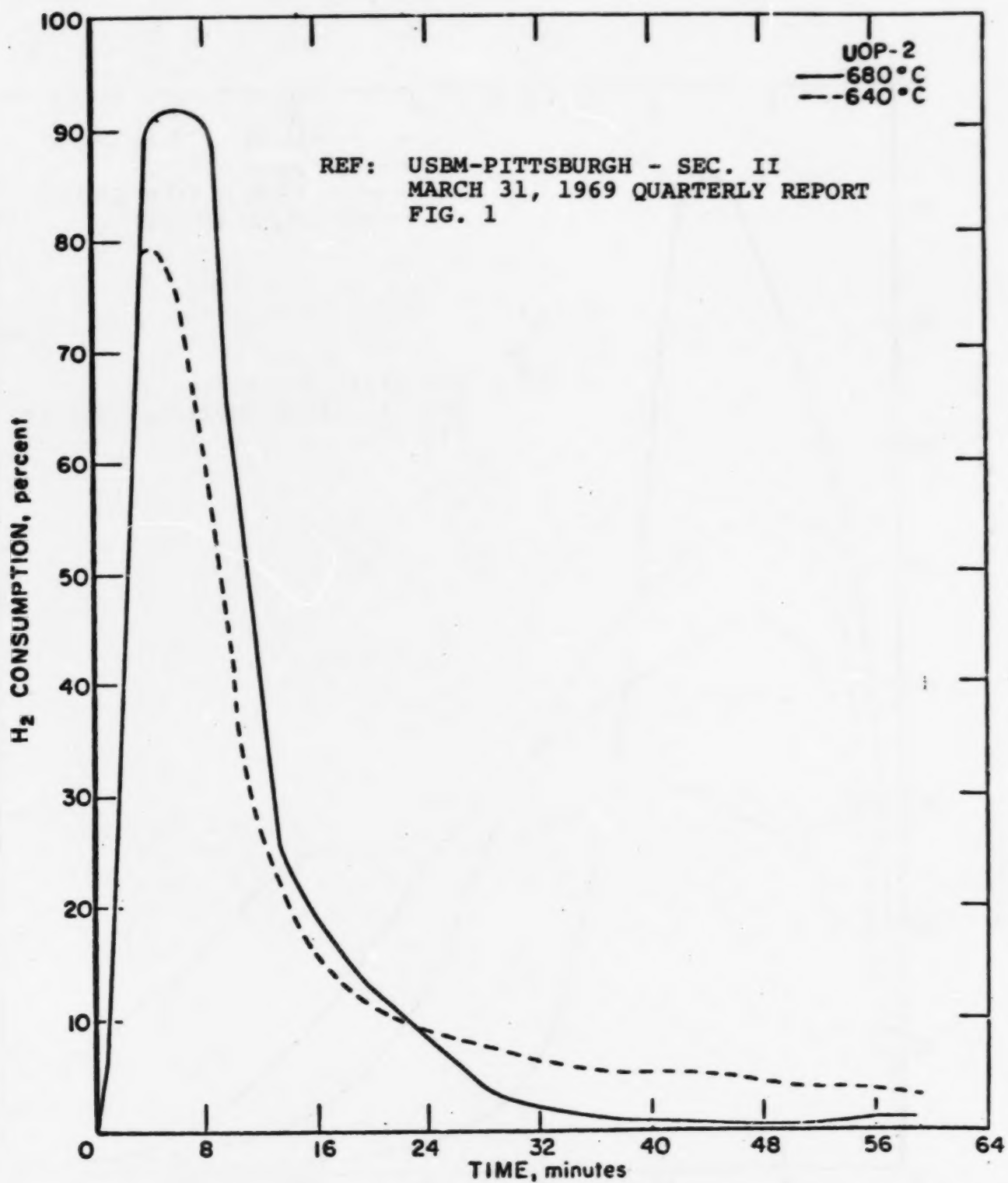


FIGURE F-88 - H₂ Regeneration of the UOP-2 Sorbent Impregnated With Sodium Aluminate and Ferric Nitrate at 1,000 hr⁻¹ Space Velocity.

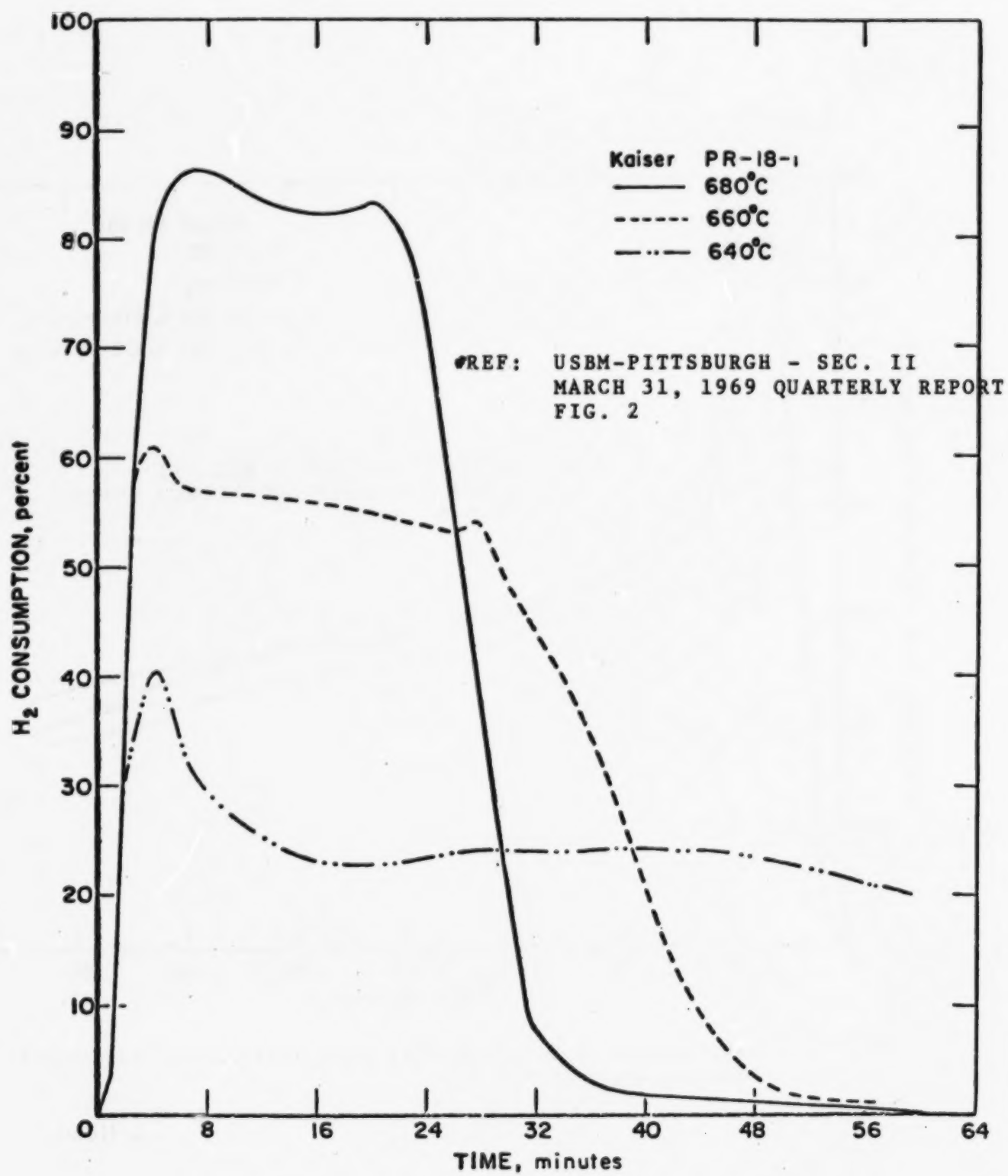


FIGURE F-89 - H₂ Regeneration of Kaiser PR-18-1 Alkalized Alumina at Three Different Temperatures and 1,000 hr⁻¹ Space Velocity.

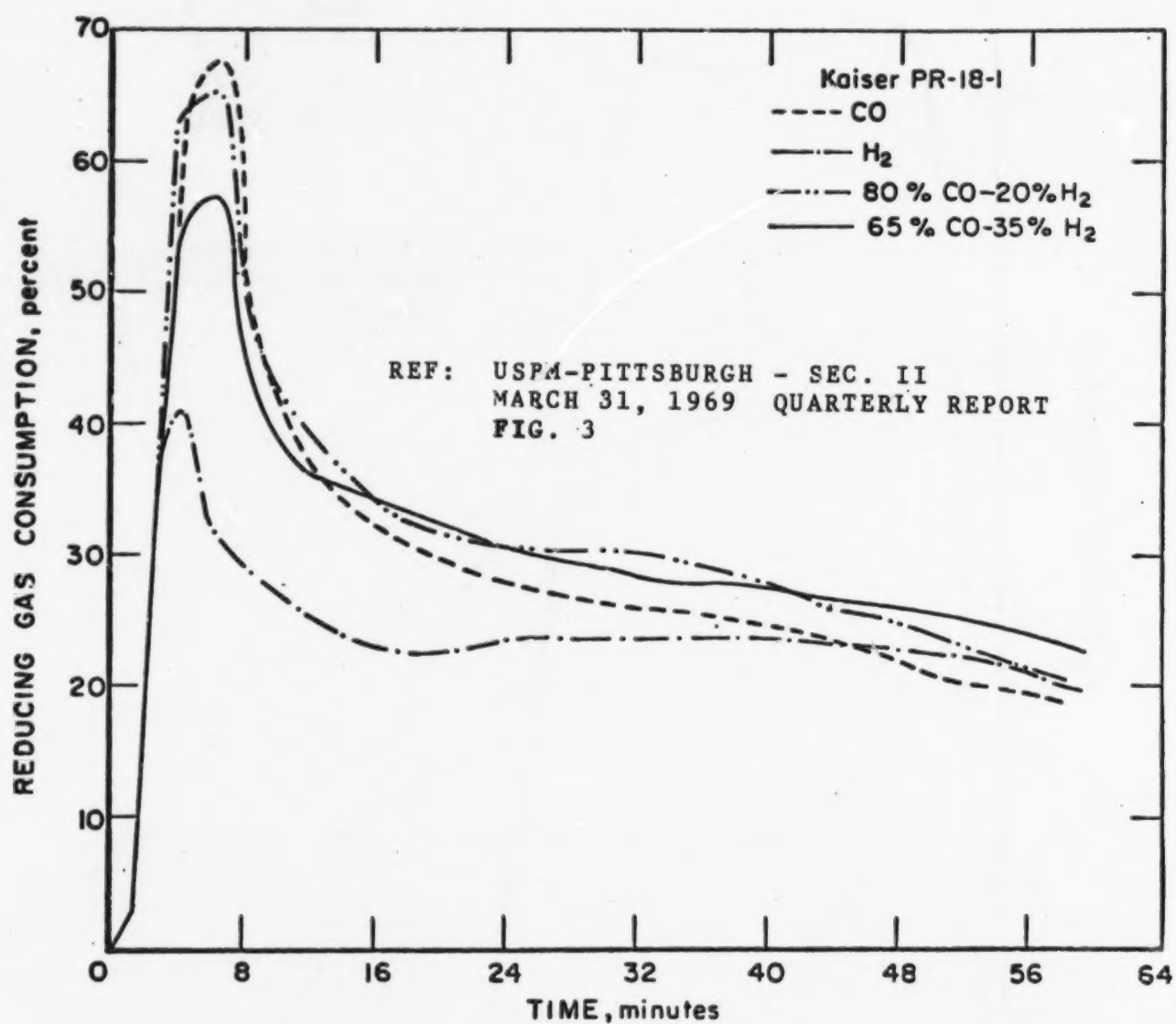
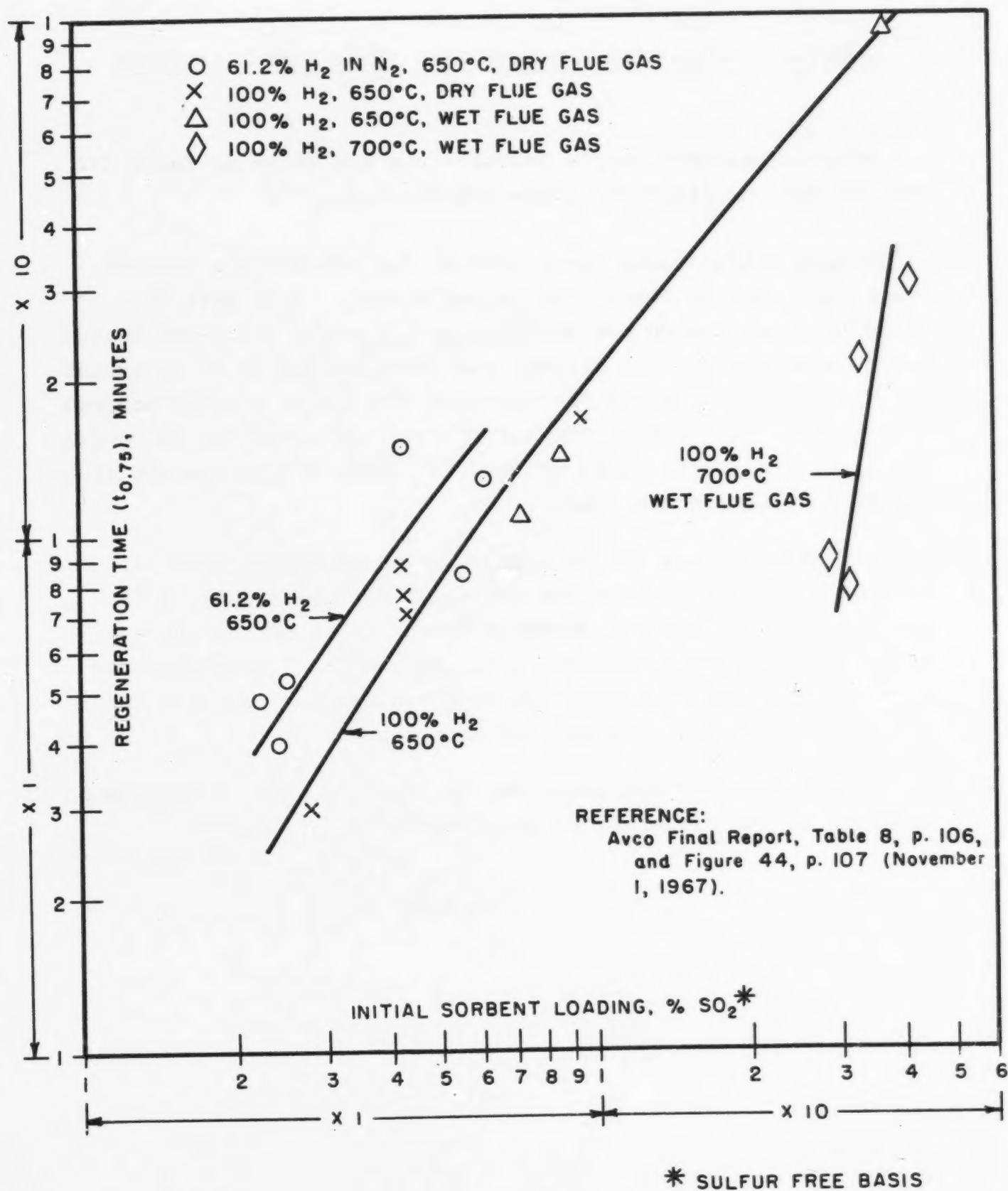


FIGURE F-90 - Regeneration of Kaiser PR-18-1 Using Various Combinations of Reducing Gases at 640° C.

L-11091

FIGURE F-91
EFFECT OF INITIAL SORBENT LOADING ON REGENERATION TIME



APPENDIX G

PROCESS CALCULATIONS AND DISPERSED PHASE VESSEL SKETCHES

Material balance sample calculations are shown in Table G82 and G83 for the dispersed phase regenerator.

Sample calculations are presented for the various methods which were used to design the solids heater. Note that the examples presented do not necessarily represent the final design but do show the various methods that were evaluated in selecting the final design. After the examples were typed several process changes were made and it was not considered worthwhile to change the sample calculations to reflect the final design numbers since the methods remain the same.

The calculations for the dispersed phase sorber material balance and vessel dimensions are shown in Tables G-89, G-90 and G-91. Note that the examples shown for sorber height are for the design which includes a solids cooler. The cooler was later deleted and extra reactor height added for heat transfer as described in the main body of this report.

Vessel sketches are shown for the major pieces of equipment required in the dispersed phase process.

TABLE G-82

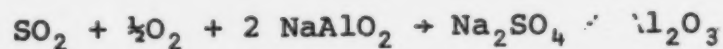
REGENERATOR MATERIAL BALANCE CALCULATIONS(1) AVCO* Regenerated Solids Product

	<u>moles</u>	<u>lbs</u>
NaAlO ₂	1.912	156.73
Al ₂ O ₃	1.479	150.80
Na ₂ SO ₄	0.044	6.25
	3.435	313.78

$$\frac{0.044(32.06)(100)}{313.78} = 0.45 \text{ wt \% S}$$

(2) Regenerated Solids Product for Design Condition of 0.5 wt % S

	<u>moles</u>	<u>lbs</u>	
NaAlO ₂	1.912	156.73	
Al ₂ O ₃	1.479	150.80	
Na ₂ SO ₄	0.049	6.97	(1.573 lbs S)
	3.440	314.50	

(3) Amount of Na₂SO₄ Formed in Absorber for Design Condition of 3 wt % S in Regenerator Feed

Let x = moles Na₂SO₄ formed in absorber
 x = moles Al₂O₃ formed in absorber
 $2x$ = moles NaAlO₂ consumed in the reaction

$$\therefore \frac{\text{wt. sulfur formed} + \text{wt. entering sulfur}}{\text{total wt. solids leaving}} = 0.03$$

*AVCO 16th Monthly Summary, April 29, 1968, Table VIII, p. 50

continued

$$\text{or, } \frac{32.06x + 1.573}{[314.50 + 142.04x + 101.96x] - 2x (81.97)} = 0.03$$

x = 0.265 moles Na_2SO_4 formed in absorber and
0.265 moles Al_2O_3 formed in absorber

(4) AVCO* Regeneration Gas Adjusted for the Above Design Conditions

	<u>AVCO</u> <u>moles</u>	<u>Factor</u>	<u>MWK</u> <u>moles</u>
H_2	3.42	0.265	0.9063
CO_2	0.58	0.265	0.1537
CO	0.444	0.265	0.1177

TABLE G-83

REGENERATION REACTION

(3 wt % S → 0.5 wt % S)

(1) Balanced Reaction

	<u>MOLS</u>
Reactants:	0.265 Na ₂ SO ₄
	0.265 Al ₂ O ₃
	0.9063 H ₂
	0.1537 CO ₂
	0.1177 CO
Products:	0.53 NaAlO ₂
	0.0022 CO
	0.0046 COS
	0.265 CO ₂
	0.0202 H ₂
	0.6491 H ₂ O
	0.2370 H ₂ S
	0.0170 SO ₂
	0.0032 S ₂

(2) Flow Rates for 80% Utilization of Regeneration Gas (1000MW Plant)

$$* \text{ S removed to off-gas} = 619.3 \frac{\text{moles}}{\text{hr}} (0.90) = 557.4 \frac{\text{moles S}}{\text{hr}}$$

$$\text{Equation Scale Factor} = 557.4/0.265 = 2103.4$$

* Table G-89

continued.....

Regeneration Gas:

<u>Component</u>	<u>moles*</u>	<u>mole fraction</u>	<u>equation scale factor</u>	<u>moles/ hr</u>	<u>lbs/hr</u>
H ₂	1.1329	0.769	2103.4	2382.9	4,813
CO ₂	0.1921	0.131	2103.4	404.1	17,784
CO	<u>0.1471</u>	<u>0.100</u>	2103.4	<u>309.4</u>	<u>8,666</u>
	1.472	1.000		3096.4	31,263

*includes 25% excess over theoretical

Regeneration Off-Gas:

<u>Component</u>	<u>moles</u>	<u>mole fraction</u>	<u>equation scale factor</u>	<u>moles/ hr</u>	<u>lbs/hr</u>
CO	0.0316	0.0212	2103.4	66.47	1,862
COS	0.0046	0.0031	2103.4	9.68	581
CO ₂	0.3034	0.2033	2103.4	638.17	28,079
H ₂	0.2468	0.1653	2103.4	519.12	1,049
H ₂ O	0.6491	0.4348	2103.4	1365.32	24,603
H ₂ S	0.237	0.1588	2103.4	498.50	16,989
SO ₂	0.0170	0.0114	2103.4	35.76	2,291
S ₂	0.0032	<u>0.0021</u>	2103.4	<u>6.73</u>	<u>432</u>
		1.0000		3139.75	75,886

$$S \text{ in Off Gas} = \frac{557.4}{3139.75} (100) = 17.75\% \text{ mole}$$

TABLE G-84

SAMPLE CALCULATION - SOLIDS HEATER DIAMETER

FOR TWO

TEMPERATURE APPROACHES

1000 MW PLANT

Conditions: 2 psig inlet pressure
 Assume 1 psig pressure drop
 0.5 ft/sec average superficial gas velocity
 75.6MM Btu/hr duty for each of 2 trains
 Assume cylindrical vessels for purposes of calculation

<u>50° APPROACH</u>	<u>10° APPROACH</u>
Solids: 600 + 1271°F Gas: 650 + 1500°F	Solids: 600 + 1271°F Gas: 610 + 1500°F
Amount of air needed: 75,600,000 = x (7.75)(1500-650) x = 11,476 moles/hr/train or 332,804 lbs/hr/train	Amount of air needed: 75,600,000 = x (7.75)(1500-610) x = 10,960 moles/hr/train or 317,840 lbs/hr/train
ACFM _{out} = $\frac{11,476(10.73)(460 + 650)}{60(15.7)}$ = 145,098	ACFM _{out} = $\frac{10,960(10.73)(460 + 610)}{60(15.7)}$ = 133,581
ACFM _{in} = $\frac{11,476(10.73)(460 + 1500)}{60(16.7)}$ = 240,868	ACFM _{in} = $\frac{10,960(10.73)(460 + 1500)}{60(16.7)}$ = 230,037
ACFM _{avg} = 192,983	ACFM _{avg} = 181,809
$\frac{192,983}{60(0.5)} = 6433 \text{ ft}^2$ cross section	$\frac{181,809}{60(0.5)} = 6060 \text{ ft}^2$ cross section
∴ Diameter = -90.5 ft for each of 2 solids heaters	∴ Diameter = -88 ft for each of 2 solids heaters

TABLE G-85

SAMPLE CALCULATION - SOLIDS HEATER BED HEIGHT

BRINN* CORRELATION

1000 MW PLANT

Conditions: 75.6 MM Btu/hr duty for each of 2 trains.
0.5 ft/sec average superficial gas velocity
Assume 1 psig pressure drop
50° approach—

Solids: 600 + 1271°F

Gas: 650 + 1500°F

1) Calculation of Total Tube Length

Feed to Regenerator = $\frac{705,792^{**}}{2}$ = 352,896 lbs/hr/train

Mean heat capacity of solids = 0.29 $\frac{\text{Btu}}{\text{lb}^\circ\text{F}}$

$$Z = \frac{(WC_p)_{\text{solids}}}{(WC_p)_{\text{gas}}} = \frac{352,896(0.29)}{332,804(\frac{7.75}{29})} = 1.15 \quad (\text{Data from Table G-84})$$

$$\frac{t_2 - t_1}{T_2 - t_1} = \frac{1271 - 600}{1500 - 600} = 0.745$$

Assume 2" ID tubes, triangular pitch

Assume U' , coefficient of heat transfer from jacket fluid to
inside tube surface = 9 Btu/hr/ft² °F (Brinn Article)

* Brinn, M. S. et.al., IEC 40, 1050 (1948)

** Table G-89.

continued.....

$k_{Al_2O_3} @ T_{avg} = 4.62 \text{ Btu/hr ft } ^\circ\text{F}$ (Thermophysical Properties Research Center, DATA BOOK, Purdue Univ., Lafayette, Indiana (1964))

$$\beta = \frac{k}{U_R} = \frac{4.62(12)}{9(1)} = 6.2$$

From the design curves (Brinn Article, Figs. 14-15-16 extrapolated)

$$\frac{wc_p}{kL} = 0.6$$

It can be seen that for appropriate values of the temperature ratio, there is a narrow spread in values for wc_p/kL for $\beta = 2$ and $\beta = 20$.

$$\frac{352,896(0.29)}{4.62(L)} = 0.6$$

$\therefore L = 36,919 \text{ ft total tube length for each of 2 solids heaters.}$

2) Calculation of Number of Tubes and Bed Height

$$N = C \left(\frac{L}{P} \right)^{2*}$$

where $C = \text{constant} = 0.86$ for triangular pitch

$P = \text{tube spacing} = 1.25(D) + 1/2 = 3 \text{ inches}$

$L = \text{outer tube limit, inches}$

(Floating Head Exchanger = Shell ID - 1-1/2")

$N = \text{number of tubes}$

* Nelson, W. L., PETROLEUM REFINERY ENGINEERING, McGraw-Hill Book Company, New York (1958).

continued.....

TABLE G-85 (continued)

∴ For 16.7 psia inlet pressure and 90.5 ft diameter vessels (2):

$$N = 0.86 \left[\frac{90.5(12) - 1.5}{3} \right]^2$$

N = 112,387 tubes for each of 2 solids heaters

∴ Bed Height = $\frac{36,919 \text{ ft total tube length}}{112,387 \text{ tubes}}$

= 0.33 ft for each of 2 solids heaters.

TABLE G-86

SAMPLE CALCULATION - SOLIDS HEATER BED HEIGHT

FURNAS* METHOD

1000 MW PLANT

- Assumptions:
- 1) Negligible resistance to heat transfer by conduction in the solid.
 - 2) Countercurrent heat exchange between a fluid and solid without heat generation within the solid.
 - 3) Area for heat exchange is the total external area of the particles in the bed at one time.
 - 4) Solid consists of uniform spheres.
 - 5) The exchanger is adiabatic, the only heat transferred being that between the solid and fluid.
 - 6) Heat conduction in the fluid in the direction of flow is negligible.

* Munro, W. D., and Amundson, N. R., IEC, 42, 1481 (1950)
Furnas, C. C., IEC, 22, 26 (1930)
Furnas, C. C., TRANS AICHE, 24, 1942 (1930)
Furnas, C. C., U. S. BUR. MINES, BULL., 361 (1932)

continued.....

Conditions: 75.6 MM Btu/hr duty for each of 2 trains.
 0.5 ft/sec average superficial gas velocity
 Assume 1 psig pressure drop
 50° Approach—

Solids: 600 + 1271°F
 Gas: 650 + 1500°F

16.7 psia inlet pressure
 90.5 ft diameter vessels (2)

$$\frac{T - t_o}{T_o - t_o} = \frac{1500 - 600}{650 - 600} = 18$$

$$\beta = \frac{G_s C_s}{G C_p} = \frac{352,896(0.29)}{332,804(7.75/29)} = 1.15 \quad \text{(Data from Tables G-84 and G-85)}$$

Based on Grace #2 Catalyst, Bruceton Quarterly, June 30, 1968:
 After 3 regenerations - 50% size = 1300μ. Further cycling will reduce this. Therefore, in these calculations, assume a 1000μ particle size.

$$\therefore R, \text{ radius of sphere} = \frac{0.10}{2(2.54)(12)} = 0.00164 \text{ ft}$$

h_f , heat transfer coefficient at solid-fluid interface:

REF: Leva, FLUIDIZATION, McGraw-Hill Book Company, New York (1959)

$$\frac{h D_p}{k} = 0.0063 \left[\frac{D_p G}{\mu} \right]^{1.8} \quad \text{(Eq. 8-53)}$$

continued.....

$$\begin{aligned} @ T_{avg} &= 1075F & k_{air} &= 0.0325 \text{ Btu/hr ft } ^\circ F \\ & & \mu_{air} &= 0.0955 \text{ lbs/hr ft} \end{aligned}$$

$$G_{air} = 332,804/6433 = 51.73 \text{ lbs/hr ft}^2 \text{ (Data from Table 1)}$$

$$\therefore h = \frac{0.0325(0.0063)}{0.00329} \left[\frac{0.00328(51.73)}{0.0955} \right]^{1.8}$$

$$h = 0.18 \text{ Btu/hr ft}^2 \text{ } ^\circ F$$

Furnas Approximate Equation*:

$$\frac{T - t_o}{T_o - t_o} = \frac{1}{1-\beta} + \frac{\beta}{\beta-1} \exp \left[\frac{3(\beta-1)\gamma x}{\epsilon R^2} \right] \text{ for } \beta \neq 1$$

$$\text{where } \epsilon = k_s/h_f R$$

$$\gamma = \frac{k_s(1-f)}{G_s C_s}$$

$$\therefore \frac{\gamma}{\epsilon} = \frac{(1-f)h_f R}{G_s C_s}$$

Let fraction voids = 0.60 = f (from MWK Progress Report No. 7, p14)

$$G_s = \frac{352,896}{6433} = 54.86 \text{ lbs/hr ft}^2 \quad \text{(Data from Tables G-84 and G-85)}$$

$$\therefore \frac{\gamma}{\epsilon} = \frac{0.40(0.18)(0.00164)}{54.86(0.29)} = 0.00000742$$

* Munro, W. D., and Amundson, N. R., IEC, 42, 1481(1950)

continued.....

$$\therefore 18 = \frac{1}{1-1.15} + \frac{1.15}{1.15-1} \exp \left[\frac{3(1.15-1)(0.00000742)x}{(0.00164)^2} \right]$$

$$18 = -6.67 + 7.67 \exp [1.2414x]$$

$x = -1.3$ ft bed height for each of 2 solids heaters

TABLE G-87

SAMPLE CALCULATION - TEMPERATURE HISTORY CURVE -
HEATING OF SOLIDS HEATER BED FOR 0.075 HRS HOLD-UP

MWK CORRELATION - 1000 MW PLANT

Conditions: 75.6 MM Btu/hr duty for each of 2 trains
0.5 ft/sec average superficial gas velocity
Assume 1 psig pressure drop
10°F approach—

Solids: 600 + 1271°F
Gas: 610 + 1500°F

16.7 psia inlet pressure
88 ft. diameter vessels (2)

1) Calculation of Convection Coefficient

$$hA = \frac{17.5 C_g (G^{0.7}) (z_g^{0.3}) (10^{1.68f-3.56f^2})}{D^{0.9}}$$

where C_g , mean specific heat of the gas, = 7.75/29 = 0.267 Btu/lb °F
 G , gas mass velocity, = 317,840/6060 = 52.4 lbs/hr ft²
 z_g , gas viscosity at average temperature, = 0.0955/2.42 = 0.039 cp
 f , fraction voids in bed, = 0.60
 D , particle diameter, = 1000μ = 0.00328 ft

(The above data are from Tables G-84 and G-86)

$$hA = \frac{17.5(0.267)(52.4)^{0.7}(0.039)^{0.3}(10^{-0.2736})}{(0.00328)^{0.9}}$$

$$hA = 2593.4 \text{ Btu/hr ft}^3 \text{ °F}$$

continued.....

2) Time - Temperature Relationship

C_s = mean heat capacity of solid = 0.29 Btu/lb °F

ρ_s = packed solids density = 45 lbs/ft³

t = hold-up time, hrs

x = bed height, ft

T_g = temperature of gas at any point at any time, °F

T_s = temperature of solid at any point at any time, °F

T_o = initial temperature of gas, °F

T_{so} = initial temperature of solid, °F

$$Z = \frac{hAt}{C_s \rho_s} = \frac{2593.4t}{0.29(45)} = 198.7t$$

$$Y = \frac{hAx}{GC_g} = \frac{2593.4x}{52.4(0.267)} = 185.4x$$

$$l_g = \frac{T_g - T_{so}}{T_o - T_{so}} = \frac{T_g - 600}{1500 - 600} = \frac{T_g - 600}{900}$$

$$l_s = \frac{T_s - T_{so}}{T_o - T_{so}} = \frac{T_s - 600}{1500 - 600} = \frac{T_s - 600}{900}$$

The following data are plotted on Figure 49:

$$t = 0.075 \text{ hrs ; } Z = 14.94$$

x(ft) Bed Ht.	Y = 185.4x	l_g	$T_g =$ $900(l_g) + 600$	l_s	$T_s =$ $900(l_s) + 600$
0.1	18.5	0.29	861	0.23	807
0.125	23.2	0.11	699	0.08	672
0.15	27.8	0	600	0	600
0.025	4.6	1.0	1500	1.0	1500
0.05	9.3	0.895	1406	0.855	1370
0.075	13.9	0.63	1167	0.535	1082

continued.....

For 0.075 hrs hold-up:

$$352,896 \frac{\text{lbs}}{\text{hr}} (0.075 \text{ hrs}) (\text{ft}^3 / 45 \text{ lbs}) (1/6060 \text{ ft}^2) = 0.097 \text{ ft bed ht.}$$

The area under the solids curve from 840°F (corresponding to 0.097 ft bed ht.) to 1500°F = 45.19 ft °F (from planimeter)

$$\therefore \text{Average solids temperature} = \frac{45.19 \text{ ft } ^\circ\text{F}}{0.097 \text{ ft}} + 840^\circ\text{F} = 1306^\circ\text{F}$$

(above the
required 1271°F)

Also shown in Figure 49 are the temperature history curves for other holdup times, viz., 0.150, 0.225 and 0.300 hours.

Figure G-92 shows the temperature history curves when the pressure is increased to 116 psia which changes the vessel diameter to 33 feet. Other conditions remain the same as in Figure 49.

FIGURE G92
TEMPERATURE — HISTORY CURVES FOR SOLIDS HEATER

MWK METHOD

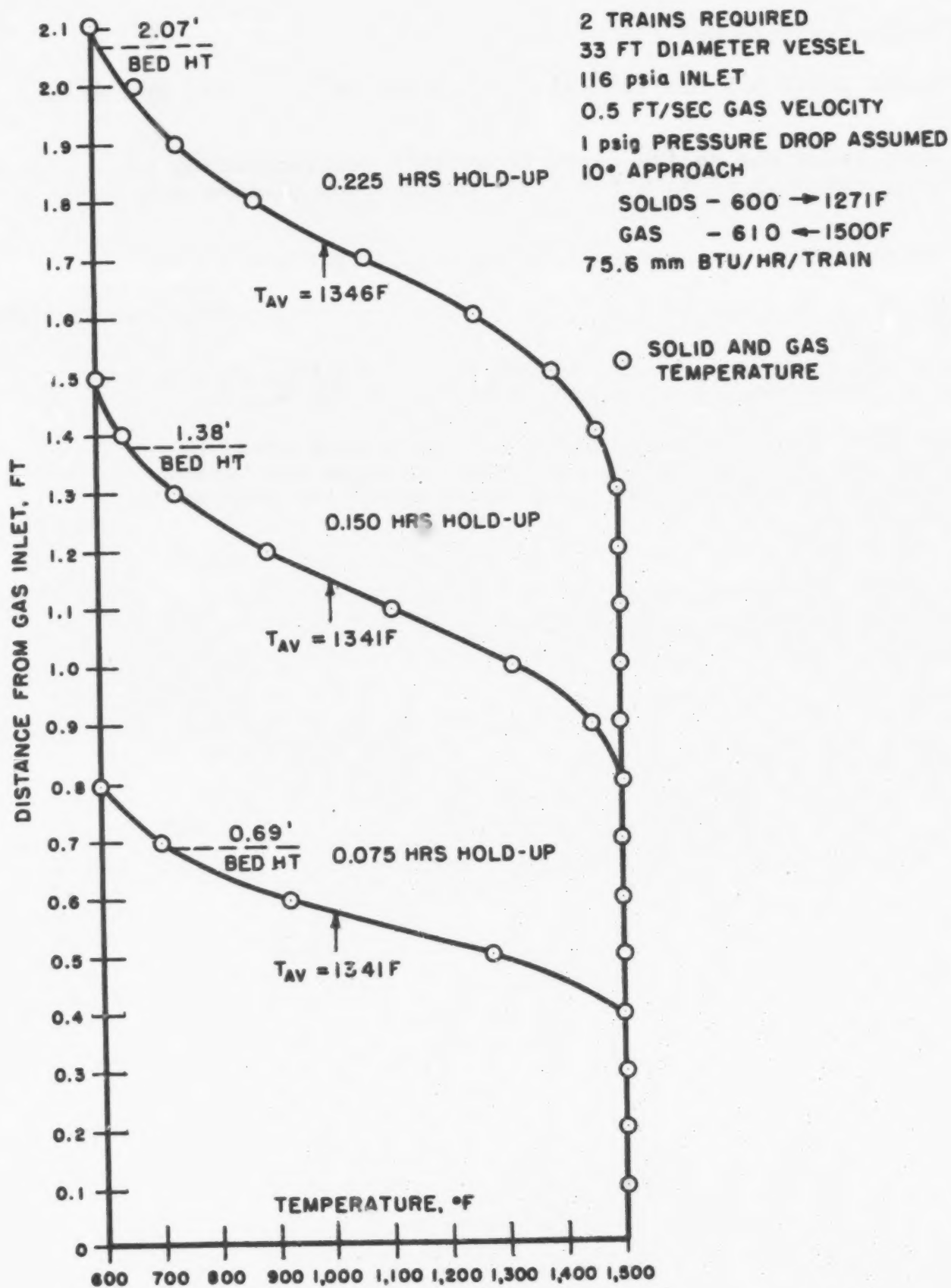


TABLE G-88

SAMPLE CALCULATION - PRESSURE DROP THROUGH SOLIDS HEATER MOVING BED

HAPPEL* CORRELATION

1000 MW PLANT

Conditions: 75.6 MM Btu/hr for each of 2 trains
0.5 ft/sec average superficial gas velocity
Initially 1 psig pressure drop assumed
50°F approach—

Solids: 600 + 1271°F
Gas: 650 + 1500°F

16.7 psia inlet pressure
90.5 diameter vessels (2)

The correlating equation is applicable to gravity flow of solids when under countercurrent or cocurrent vapor flow, as long as the solids velocity relative to the wall is not in excess of 20% of the vapor velocity. For moving beds with solids linear velocities exceeding 20% of the superficial gas velocity, it is suggested that the correlation be modified by substituting fluid velocity relative to the moving particles, rather than relative to the vessel wall.

Check to see if $V_s > 0.20V_g$

$$V_s = \frac{54.86 \text{ lbs/hr ft}^2}{45 \text{ lbs/ft}^3 (3600 \text{ sec/hr})} = 0.00034 \text{ ft/sec} \quad (\text{Data from Tables G-86})$$

$$V_g = 0.5 \text{ ft/sec}$$

$\therefore V_s \nless 0.20V_g$ and correlation is applicable without modification.

* Happel, J., IEC, 41, 1161 (1949)
Leva, M., FLUIDIZATION, McGraw-Hill Book Company, New York (1959)

continued.....

$$\text{Modified Re} = \frac{D_p G (1-\epsilon)}{\mu}$$

where D_p , composite particle diameter = $1000\mu = 0.0394$ in.
(Data from Table G-86)

G , air mass velocity = 51.73 lbs/hr/ft²

ϵ , bed voidage = 0.60

μ , air viscosity = 0.0955 lbs/hr ft

$$\therefore \text{Modified Re} = \frac{0.0394 (51.73) (0.4)}{0.0955 (12)} = 0.711$$

$$\Delta P = \frac{f_M 2L u_o^2 \rho_f (1-\epsilon)^3}{g_c D_p} \quad (\text{Leva*}, \text{ pl64, Eq. 6-20})$$

where f_M , modified friction factor = 2500 (Leva*, pl64, Fig. 6-14)

u_o , superficial gas velocity = 0.5 ft/sec

$\rho_{f_{avg}}$, fluid density = $\frac{16.2 (29)}{10.73 (460 + 1075)} = 0.029$ lbs/ft³

L , bed height; Use 3 ft since maximum calculated bed height was 3 ft.

$$\therefore \Delta P = \frac{2500 (2) (3) (0.5)^2 (0.029) (0.4)^3}{32.2 (0.0394)} \left[\frac{12}{144} \right]$$

$$\Delta P = 0.46 \text{ psig (O.K. since less than 1 psig assumed)}$$

* op. cit.

TABLE G-89
DISPERSED PHASE ABSORBER MATERIAL BALANCE
1000 MW PLANT

1) Feed Rate to Absorber

$$x_f = \frac{x_o L_f + 0.0893 (y_o - y_f) V}{L_f + 0.2230 (y_o - y_f) V}$$

(Ref: USBM Quarterly
Report - Section I -
March 31, 1968 - Eq. 17)

where $(y_o - y_f)$ = mole fraction SO_2 in flue gas removed

MPH SO_2 in flue gas initially* = $0.002146(288,583) = 619.3$ MPH

∴ for 90% removal of SO_2 ,

$$(y_o - y_f) = \frac{619.3(0.90)}{288,583} = 0.001931$$

V = SCFH flue gas

$$V = 62,012 \frac{ft^3}{sec} \times \frac{3600 sec}{hr} \times \frac{492^\circ R}{1060^\circ R} = 103,618,542$$

x_o = weight fraction S in sorbent** feed = 0.005

x_f = weight fraction S in sorbent leaving absorber = 0.03

L_f = sorbent feed rate, lbs/hr

∴ Substituting into the above equation gives

$$0.03L_f + 0.03(0.2230)(0.001931)(103,618,542) = 0.005L_f + 0.0893(0.001931)(103,618,542)$$

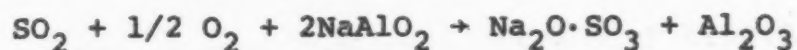
$$\text{and } L_f = 661,169 \text{ lbs/hr}$$

2) Total Feed to Regenerator

Sulfur removed in Absorber:

$$619.3 \frac{\text{moles}}{\text{hr}} \times 32.06 \frac{\text{lbs}}{\text{mole}} \times 0.90 = 17,869 \text{ lbs S/hr}$$

Sorbent weight gain as SO_3 :



$$17,869 \frac{\text{lbs S}}{\text{hr}} \times \frac{80.06 \text{ lbs SO}_3/\text{mole}}{32.06 \text{ lbs S/mole}} = 44,623 \text{ lbs SO}_3/\text{hr}$$

Sulfur in Absorber Fresh Feed:

$$0.005 (661,169) = 3306 \text{ lbs S/hr}$$

Sulfur in Feed to Regenerator:

$$3306 + 17,869 = 21,175 \text{ lbs S/hr}$$

Total Feed to Regenerator:

$$661,169 + 44,623 = 705,792 \text{ lbs/hr}$$

* Table H-96.

** Sorbent weight is defined as the total weight of solid, including the absorbed sulfur oxides.

TABLE G-90

EXPRESSION FOR DISPERSED PHASE ABSORBER HEIGHT

$$c = 3/h (y_o^{1/3} - y_f^{1/3}) \quad (\text{Eq. 13})$$

$$\bar{r} (x_o + x_f) = 2K \left[y_o - 1/2 c y_o^{2/3} h + \frac{1}{9} c^2 y_o^{1/3} h - \frac{1}{108} c^3 h^3 \right] \quad (\text{Eq. 16})$$

$$\bar{r} = \frac{0.0342 (y_o - y_f) V}{P a} \quad (\text{Eq. 6})$$

$$x_f = \frac{x_o L_f + 0.0893 (y_o - y_f) V}{L_f + 0.2230 (y_o - y_f) V} \quad (\text{Eq. 17})$$

$$P = 0.1924 h \rho \quad (\text{Eq. 4})$$

Combining the above equations gives, for 90% SO₂ removal:

$$h = \left[\frac{x_o L_f + 0.0804 y_o V}{L_f + 0.2007 y_o V} + x_o \right] \left[\frac{V}{5.562 K a \rho} \right]$$

where h = absorber height, ft
 x_o = weight fraction sulfur in sorbent feed
 L_f = sorbent feed rate, lbs/hr
 y_o = mole fraction SO₂ in flue gas to absorber
 V = flue gas flow rate, SCFH
 a = absorber cross-sectional area, ft²
 ρ = average sorbent density, lbs/ft³
 K = rate constant, hours⁻¹

Ref: USBM Quarterly
 Report - Section I -
 March 31, 1968

TABLE G-91
SAMPLE CALCULATION - ABSORBER DIMENSIONS
1000 MW PLANT

Absorber inlet flue gas
 (600°F, 14.7 psia) = 62,012 $\frac{\text{ft}^3}{\text{sec}}$ (Table H-96)

Desired superficial gas velocity = 25 ft/sec

∴ Absorber cross sectional area = $\frac{62,012}{25} = 2481 \text{ ft}^2$

Initially, assume a maximum vessel diameter of 40 ft; $a = 1256 \text{ ft}^2$
 therefore, 2 - 40 ft diameter absorbers are required.

Calculate absorber height from equation in Table G-90 for 90% SO₂ removal:

$$h = \left[\frac{x_o L_f + 0.0804 y_o V}{L_f + 0.2007 y_o V} + x_o \right] \left[\frac{V}{5.562 K a \rho} \right]$$

$x_o = 0.005$ (wt fract S in sorbent feed)

$y_o = 0.002146$ (mol fract SO₂ in entering flue gas)

$\rho = 0.15 \text{ lbs/ft}^3$ (average sorbent density)

$K = 22 \text{ hrs}^{-1}$ rate constant at 10/1 recycle ratio calculated from USBM linear sorbent loading model, USBM-Bruceton Quarterly Report, March 31, 1968).

Since 2 - 40 ft diameter absorbers are required, use 1/2 the flow rates from Table

$a = 1256 \text{ ft}^2$ cross sectional area

$L_f = 661,169/2 = 330,585 \text{ lbs/hr}$

$V = 103,618,542/2 = 51,809,271 \text{ SCFH flue gas}$

continued

Substituting these design conditions into the above equation gives:

$$h = \left[\frac{0.005 (330,585) + 0.0804 (0.002146) (51,809,271)}{330,585 + 0.2007 (0.002146) (51,809,271)} + 0.005 \right]$$

$$\times \left[\frac{51,809,271}{(5.562) (1256) (22) (0.15)} \right]$$

$$h = (0.035) (2247.36) = 78.66$$

$$\therefore h = 80 \text{ ft}$$

2 absorbers are needed, each 40 ft diameter x 80 ft high.

TABLE G-92
SAMPLE CALCULATION FOR SOLIDS HEATER
1000 MW PLANT

2. 2-Stage Direct Combustion Fluid Bed Solids Heater

The solids heater duty was calculated to be 90.1MM Btu/hr/train based on the following conditions:

- Regenerator feed is heated from 600 → 1400°F.
- One exchanger train required for each regenerator, or a total of two trains. Quantities shown are for each of two trains.
- Heat loss based on 100°F ΔT between the vessel and ambient air, wind velocity of 20 miles/hr, and an estimated solids cooler size, is essentially negligible.
- The duty shown above includes a 10% excess over theoretical for process uncertainties.
- The two stages are assumed to be equilibrium stages; therefore the temperature of the gas and solids leaving each stage are identical.

By trial and error, the exit gas temperature is found to be 1000°F from which the natural gas fuel and combustion air quantities can be calculated.

Solids: $Q = 90.1\text{MM Btu/hr}$
 $T = 600 \rightarrow 1400^\circ\text{F}$

Gas: Air @ 1000°F + natural gas @ 100°F @ inlet
Flue Gas @ 680°F @ exit

continued

The assumed composition of natural gas and air and the calculated flue gas composition are:

NATURAL GAS		AIR			FLUE GAS		
	% MOLE	COMPONENT	% MOLE	MOLES MOLE N.G.	COMPONENT	% MOLE	MOLES MOLE N.G.
CH ₄	95.85	O ₂	20.105	2.072	CO ₂	9.26	1.050
C ₂ H ₆	2.50	N ₂	76.095	7.842	N ₂	69.25	7.848
C ₃ H ₈	0.43	H ₂ O	3.80	0.392	H ₂ O	21.49	2.435
C ₄ H ₁₀	0.32		100.00	10.306		100.00	11.333
C ₅ H ₁₂	0.20						
C ₆ H ₁₄	0.10	M.W. = 28.41 lbs/mole			M.W. = 27.34 lbs/mole		
N ₂	0.60						
	100.00						

Using the above and total molal enthalpies, the heat available from combustion of the natural gas is calculated to be 307,000 Btu/mol with a first stage exit temperature of 1400°F.

Balance around bottom stage (by trial & error) is 73.5MM Btu/hr.

∴ Nat. gas rate = 73,500,000/307,000 = 240 mols/hr

Air req'd = 10.306 (240) = 2473 mols/hr

4 psig pressure drop assumed through solids heater.

5 ft/sec average superficial gas velocity chosen.

For a 30 psia inlet pressure:

$$\begin{aligned} \text{ACFS}_{\text{in}} &= 2473 \text{ MPH Air @ } 1000^{\circ}\text{F} + 240 \text{ MPH N.G. @ } 100^{\circ}\text{F} \\ &= \frac{10.73 [2473 (1460) + 240 (560)]}{3600 (30)} = 372 \end{aligned}$$

Flue Gas Leaving = 11.333(240) = 2720 moles/hr @ 680°F

$$\text{ACFS}_{\text{out}} = \frac{2720 (10.73) (1140)}{3600 (26)} = 355$$

$$\text{Cross Sectional Area} = \frac{(372 + 355)/2}{5} = 72.7 \text{ ft}^2 \approx 10 \text{ ft dia.}$$

$$\text{Vessel Height (Table 1)} = 5 + 10 + 5 + 1 + 3.5(10) = 56 \text{ ft.}$$

∴ A 2-stage Fluid Bed Direct Combustion Solids Heater, 10'φ x 56', is required at 30 psia.

TABLE G-93

FIRST STAGE TEMPERATURE PROFILE FOR 3-STAGE
FLUID BED SOLIDS HEATER - 1000 MW PLANT

Conditions: 90.1MM Btu/hr duty for each of 2 trains
Solids: 600 + 1400°F
Gas: 990 + 1500°F; 825 lbs/hr ft² (air + flue gas)
5 ft/sec average superficial gas velocity
1 psig pressure drop assumed
30 psig inlet pressure
31 ft. diameter vessels
1000μ (0.00328 ft) diameter spherical particles
assumed.

REF: Frantz, J. F., Chem. Eng. Prog., 57 (7), 35 (1961)

$$\ln \frac{(t_g - t_s)_i}{(t_g - t_s)_o} = \frac{-ah}{C_p G} L$$

where t_{gi} = point gas temperature, °F
 t_{si} = point solids temperature, °F
 t_{go} = inlet gas temperature, °F
 t_{so} = outlet solids temperature for countercurrent case, °F
 a = surface area/unit volume, ft²/ft³
 h = heat transfer coefficient at solid-fluid interface,
Btu/hr ft² °F
 C_p = gas heat capacity, Btu/lb °F
 G = gas mass flow rate, lbs/hr ft²
 L = bed height, ft

continued.....

$$h = 0.0063 \frac{k}{D_p} \left(\frac{D_p G}{\mu} \right)^{1.8} \quad (\text{Leva, FLUIDIZATION, Mc-Graw Hill Book Co., New York (1959)})$$

$$\text{where } k = 0.0356 \text{ Btu/hr ft } ^\circ\text{F} \\ \mu = 0.0983 \text{ lbs/hr ft}$$

$$\therefore h = \frac{0.0063(0.0356)}{0.00328} \left[\frac{0.00328(825)}{0.0983} \right]^{1.8}$$

$$h = 26.7 \text{ Btu/hr ft}^2 \text{ } ^\circ\text{F}$$

$$a \text{ for sphere} = \frac{\pi D_p^2 / \text{particle}}{\frac{\pi D_p^3}{6} / \text{particle}} = \frac{6}{D_p} = \frac{6}{0.00328} = 1829.27 \text{ ft}^{-1}$$

$$C_p = 0.29 \text{ Btu/lb F}$$

$$\therefore \frac{ah}{C_p G} = \frac{1829.27 (26.7)}{0.29 (825)} = 204.14 \text{ ft}^{-1}$$

$$(t_g - t_s)_0 = 1500 - 1400 = 100^\circ\text{F} \quad (\text{1st stage})$$

The 1st stage bed temperature will be assumed equal to the 1st stage exit gas temperature $\therefore t_{s_i} = 1400^\circ\text{F}$

$$\therefore \ln \frac{t_{g_i} - 1400}{100} = 204.14L$$

Figure 51 is a plot of gas temperature vs. bed height for the first stage, the temperature profile predicted by this equation. A bed height of less than 0.3 inch per stage is required to heat the solids to 1400°F using 1500°F inlet gas.



JOB No. 6045
PAGE 23
DATE 3-18-69
BY AGS

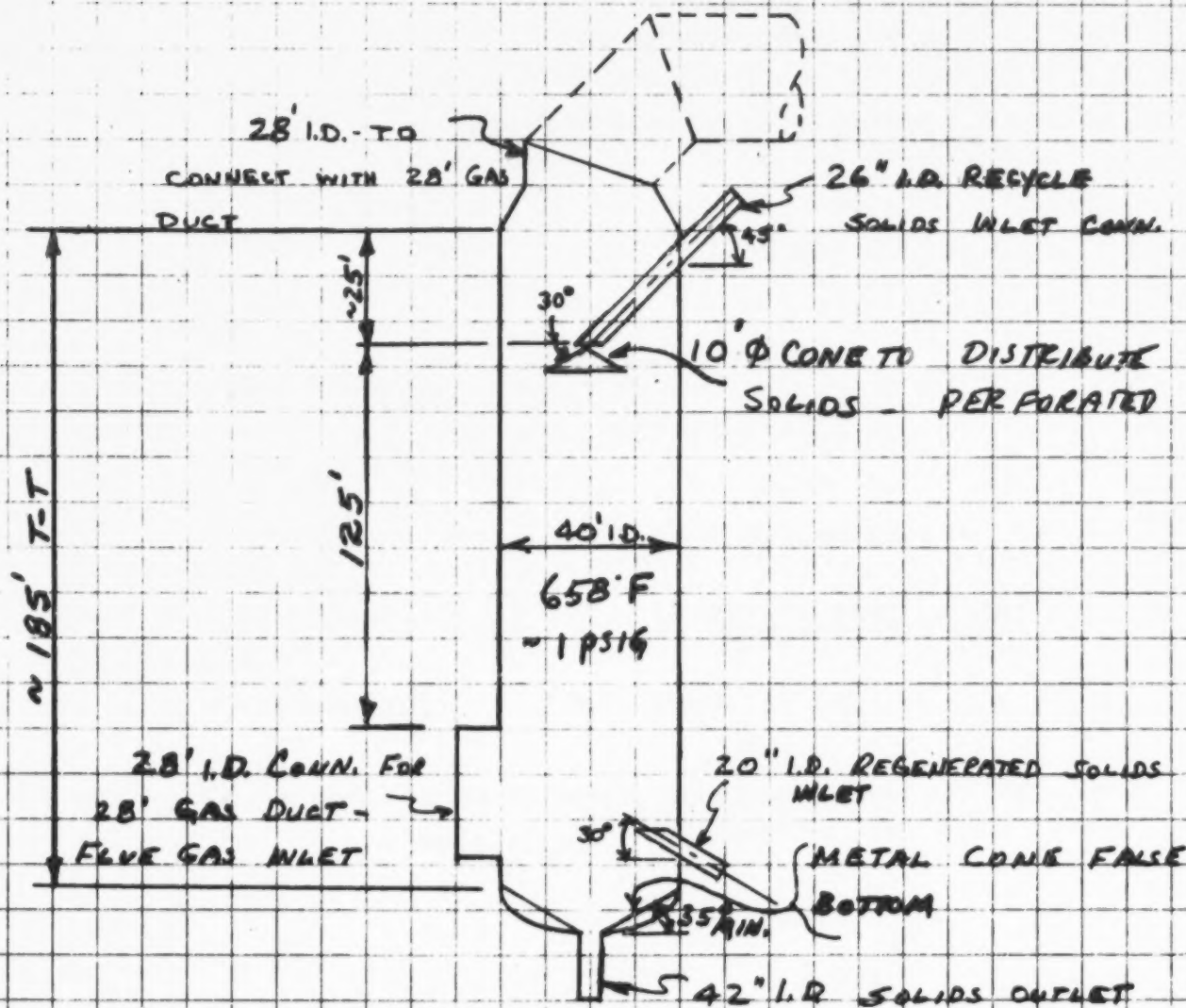
FOR NAPCA

LOCATION

SUBJECT DISPERSED PHASE DESIGN

FIGURE G-93

D-1 REACTOR - 1 REQ'D PER TRAIN - TOTAL OF 2



NOTES: MATERIAL - CARBON STEEL LINED WITH 6" THICK CASTABLE[®] GUNITE; ALL SURFACES COVERED EXCEPT FALSE BOTTOM METAL CONE

* SAME AS FOR FIXED-BED CASE

FOR **NAPCA**

LOCATION

SUBJECT **DISPERSED PHASE DESIGN**



FIGURE G-94

JOB NO **6045**

PAGE **92**

DATE **3-26-69**

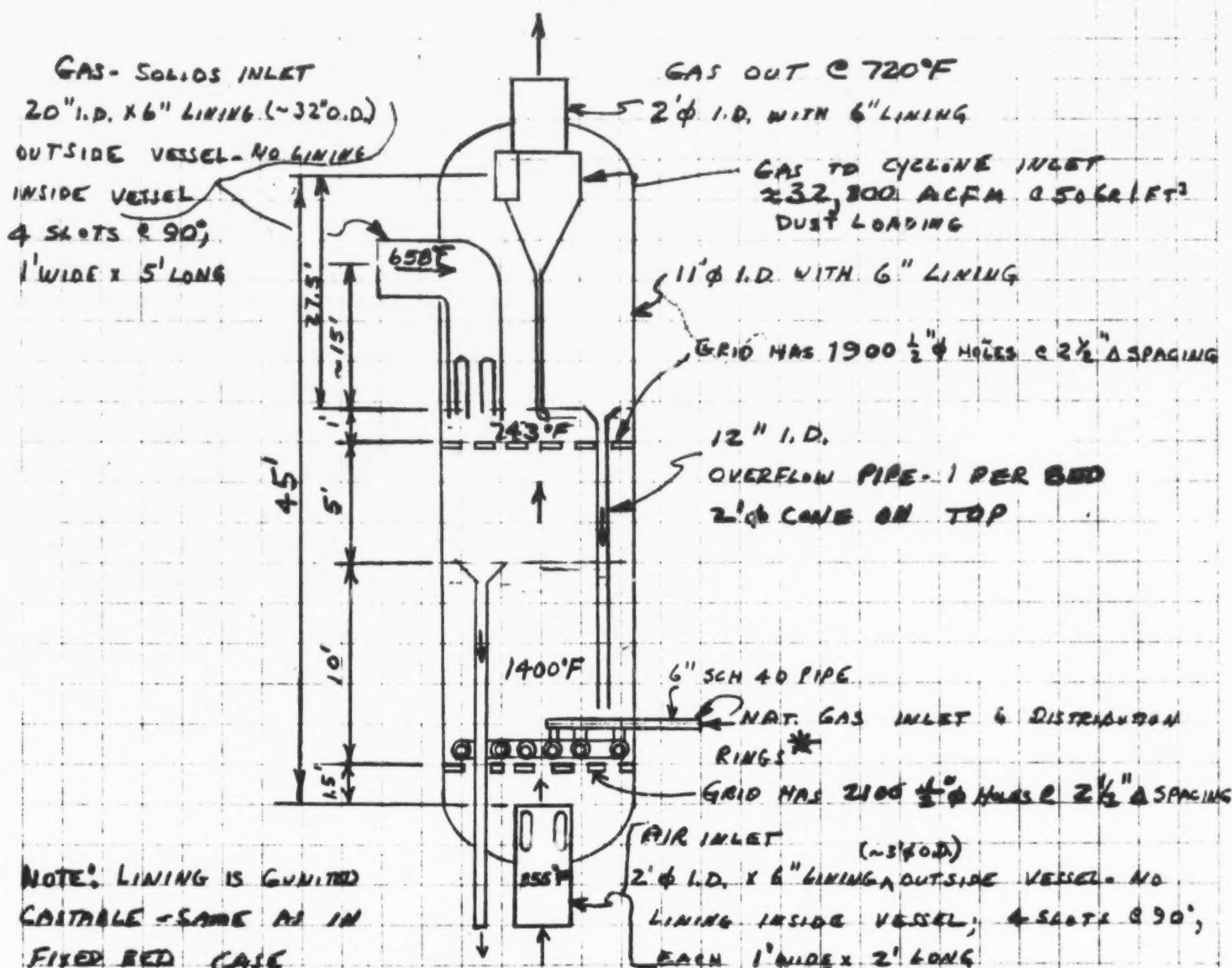
BY **AGS**

REV-1 4-11-69

D-2 FLUID BED SOLIDS HEATER

1 RECD PER TRAIN - TOTAL OF 2

DUTY - TO HEAT 353,000 LBS/HR OF SOLIDS FROM 650°F TO 1400°F IN TWO STAGES: 1 STAGE DIRECT COMBUSTION OF NAT GAS IN BED @ 1400°F; 1 STAGE HEAT EXCHANGER BETWEEN EXIT GAS & ENTERING SOLIDS



NOTE: LINING IS GUNITED CASTABLE - SAME AS IN FIXED BED CASE

P = 30 PSIA

TEMP = 1400°F BTM BED & EXIT SOLIDS

= 743°F TOP BED

= 720°F EXIT GASES

- 3 DISTRIBUTION RINGS REQUIRED:
1. 4" PIPE, 9' L, 110 - 1/4" HOLES
 2. 3" PIPE, 5' L, 65 - 1/4" HOLES
 3. 1 1/2" PIPE, 1' L, 20 - 1/4" HOLES

-G433-

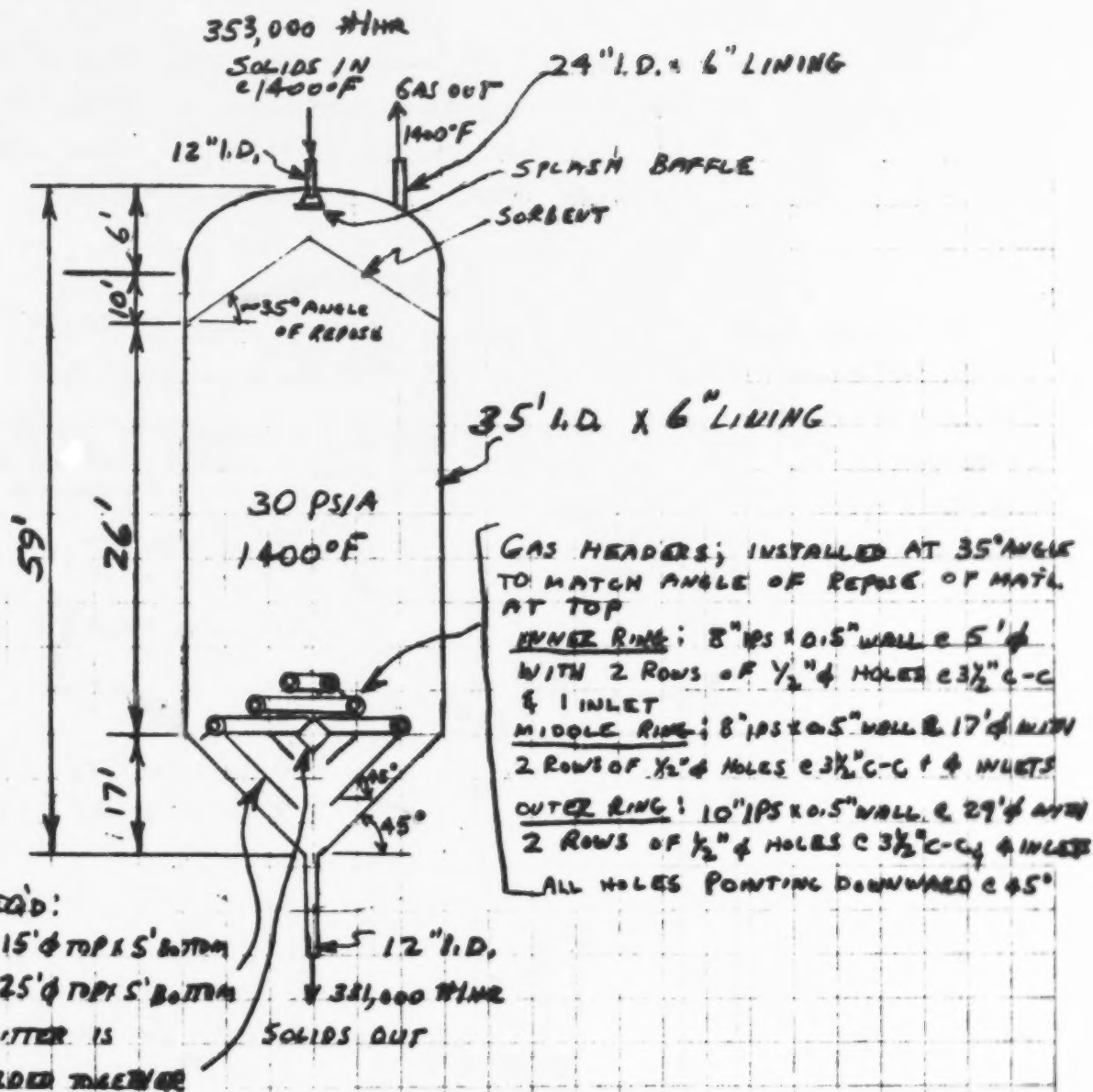
NAPCA

DISPERSED PHASE DESIGN

D-3 MOVING BED REGENERATOR

1 REQ'D. PER TRAIN = TOTAL OF 2

FIGURE G-95



NOTE: LINING IS LIMITED CASTABLE - SAME AS FIXED BED CASE
METAL IN CONTACT WITH GAS SHOULD BE 321 SS.
DIMENSIONS SHOWN ARE I.D. OF LINING

MAX. WEIGHT OF SORBENT IN VESSEL = 1,500,000 lbs

FOR **NAPCA**

LOCATION

SUBJECT **Dispersed Phase Design**



DATE **6095**

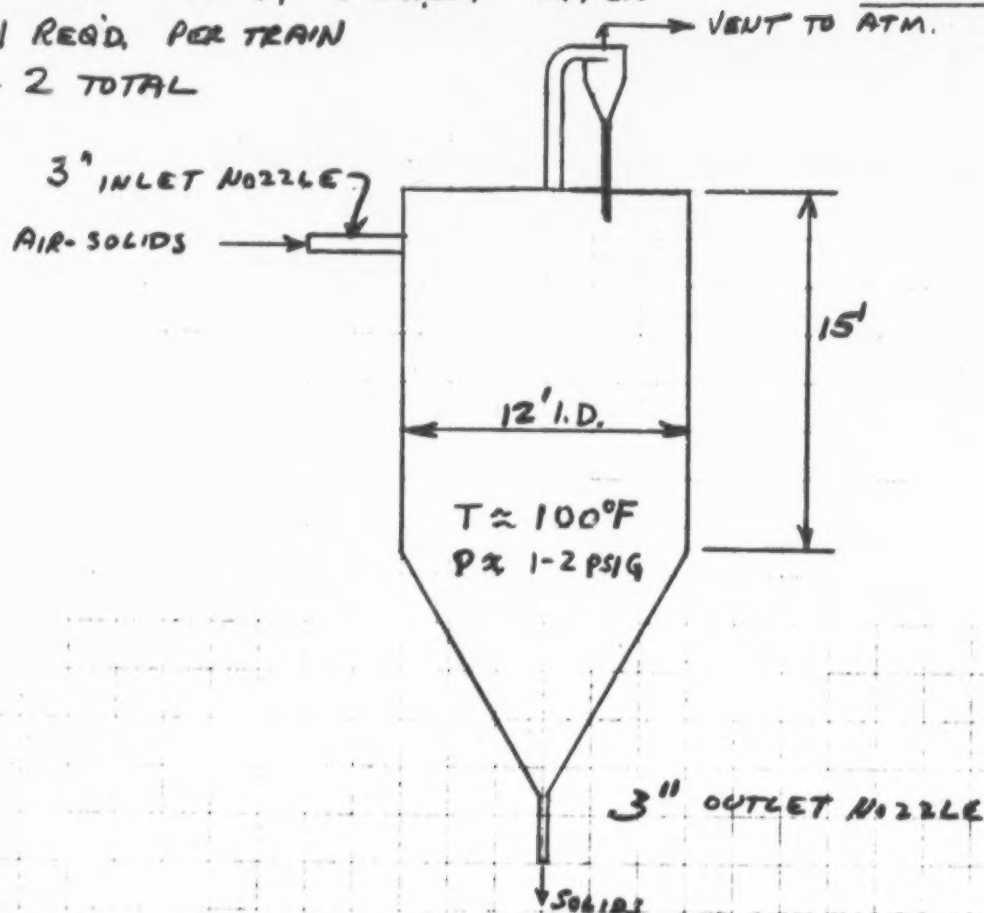
PAGE **1/3**

DATE **4-7-69**

BY **AG**

F-2 MAKE-UP SOLVENT HOPPER
1 REQ'D PER TRAIN
= 2 TOTAL

FIGURE G-96



MATERIAL - CARBON STEEL
CYCLONE CAPACITY = 300 CFM @ 60 PSI/SEC
MAX WT. MATERIAL IN VESSEL = 94,000 lbs.

FOR NAPCA

LOCATION

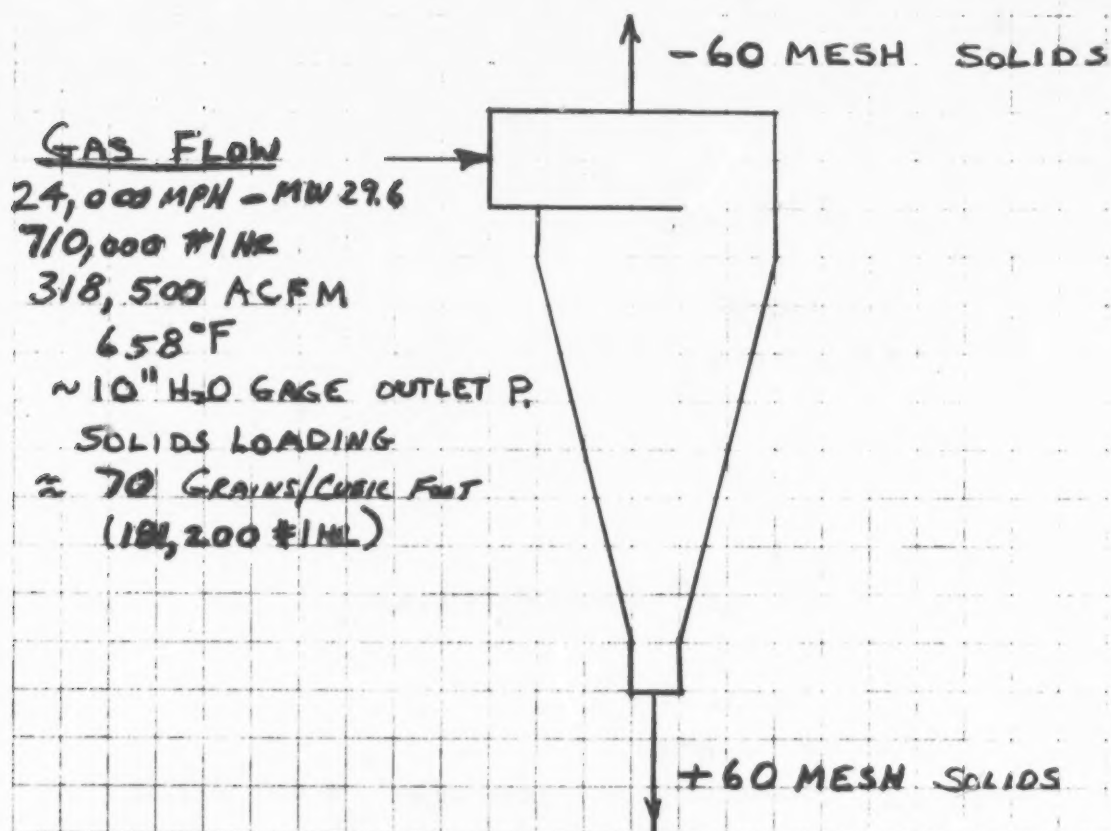
SUBJECT DISPERSED PHASE DESIGN FIGURE G-97



JOB NO. 6045
PAGE 78
DATE 3-21-69
BY AGS

FINES RECOVERY CYCLONES L-1A → L-1F (PER TRAIN)
TOTAL OF 12 REQUIRED

QUANTITIES SHOWN ARE FOR EACH CYCLONE



WANT RECOVERY OF SOLIDS $\geq 99.97\%$

MATERIAL - CARBON STEEL LINED THROUGHOUT WITH 6 INCH
CASTABLE* - GUNITED

* SAME AS FOR FIXED BED CASE

FOR NARCA

LOCATION

SUBJECT DISPERSED PHASE DESIGN

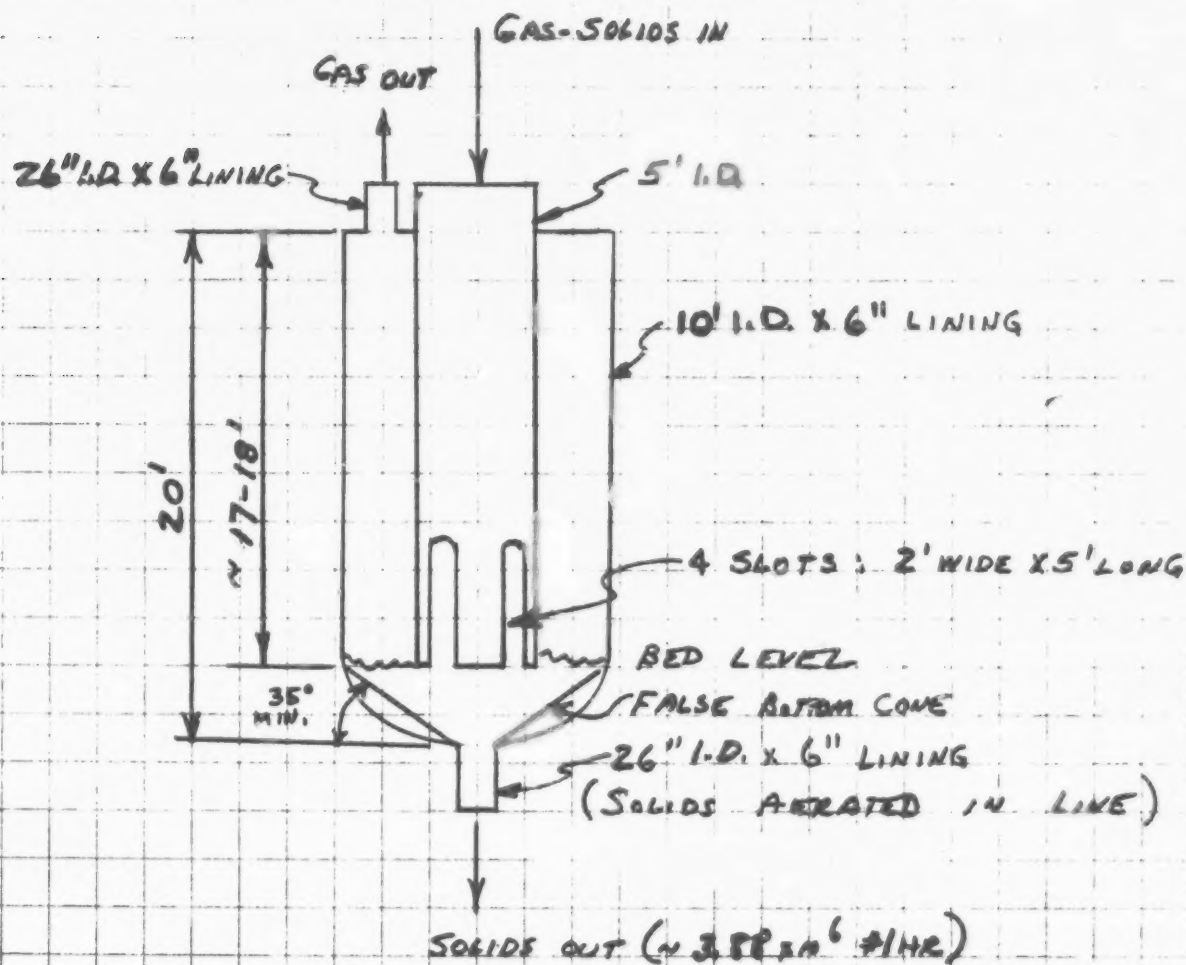
FIGURE G-98



JOB NO. 6045
PAGE 82
DATE 3-24-69
BY AGJ

L-2 GAS-SOLIDS SEPARATOR- RECYCLE LINE

1 REQD PER TRAIN = TOTAL OF 2



NOTES: MATERIAL- CARBON STEEL LINED WITH 6" THICK GUINTE
CASTABLE WHERE INDICATED, USE SAME CASTABLE
AS FOR FIXED BED CASE.

TEMP = 658°F
PRESS = 1 PSIG

APPENDIX H

COMPOSITION OF COAL AND FLUE GASES

A discussion is presented of the methods used to derive the volume and composition of the flue gases from a coal-fired power station needed for the design of the alkalized alumina processes.

APPENDIX H

COAL PROPERTIES AND FLUE GAS COMPOSITIONS

Typical flue gas volumes and compositions resulting from the burning of coal containing 1, 3, and 5% sulfur have been calculated; coal properties were estimated from analyses covering a wide range of coals. The calculations are based on a 1000 MW coal-fired power plant with an assumed heat rate of 8,600 Btu/kwh (39.7% thermal efficiency). The sources of the coal analyses are as follows:

1. MWK Progress Report #1 Contract #14-01-0001-380
2. MWK Progress Report #8 Contract #14-01-0001-380
3. Babcock & Wilcox Co., Steam-Its Generation & Use, 1955, p. 4-A5
4. USBM (Illinois), RI 5270, 1956, pp. 9-14
5. USBM (New Mexico), RI 5270, 1956, pp. 22-23
6. USBM (Wyoming), RI 5270, 1956, pp. 48-49
7. USBM (Utah), RI 5270, 1956, p. 36
8. USBM (Ohio), RI 5270, 1956, pp. 24-25

The proximate and ultimate analyses taken from these references as well as that used by S. Katell, USBM-Morgantown, in his economic study, Report #64-9, 1965 (9), are shown in Table H-94.

Based upon the analyses in Table H-94 the following analyses were taken as typical of 1, 3, and 5% sulfur coals:

<u>% S IN COAL</u>	<u>H₂O</u>	<u>ASH</u>	<u>S</u>	<u>H</u>	<u>C</u>	<u>N</u>	<u>O</u>	<u>Btu</u>
1.0	2.0	9.0	1.0	5.2	74.4	1.4	7.0	13,000
3.0	2.0	9.0	3.0	5.2	72.4	1.4	7.0	13,000
5.0	2.0	9.0	5.0	5.2	70.4	1.4	7.0	13,000

Using these analyses, the calculation of a theoretical flue gas resulting from the burning of these coals was obtained. The calculations assumed that the coals were burned using 20% excess air, the air was at 80°F and 60% relative humidity, all carbon was converted to CO₂, all hydrogen to H₂O, all sulfur to SO₂, and the air was 21% mole O₂. A typical calculation is outlined in Table H-95. The results of these calculations are given in Table H-96 showing the physical properties of the flue gas generated by the combustion of these three grades of sulfur bearing coals.

TABLE H-94

TYPICAL COAL ANALYSES

REFERENCE	PROXIMATE				ULTIMATE					Btu		
	H ₂ O	VOLATILE	F.C.	ASH	S	H	C	N	O	ASH	AS REC'D	DRY
1	2.5	39.0	53.4	5.1	1.3	5.2	79.4	1.4	7.5	5.2	13,990	14,350
2	1.31	37.3	57.59	3.8	0.66	5.14	83.6	1.48	5.27	3.85	--	--
3	8.0	--	--	-	1.6	4.4	72.0	1.4	3.6	9.0	12,800	--
4	12.2	40.3	48.8	11.0	3.4	5.0	70.4	1.4	9.3		11,130	12,720
5	13.2	41.5	47.2	11.3	1.0	5.2	70.3	1.3	12.6		10,780	12,410
6	13.1	42.7	51.2	6.2	0.7	5.3	75.6	1.4	13.3		11,210	12,800
7	3.8	43.3	48.8	8.0	0.4	5.6	75.4	1.4	10.0		12,800	13,300
8	3.0	43.1	49.5	7.4	4.2	5.2	74.3	1.3	7.6		13,260	13,680
9	1.3	--	--	12.7	3.0	4.9	70.1	1.4	6.6		--	--

TABLE H-95

SAMPLE CALCULATION FOR A 1% SULFUR COAL

	<u>M. W.</u>	<u>#</u>	<u>MOLS</u>	<u>O₂ FACTOR</u>	<u>REQUIRED O₂</u>
C	12.01	74.4	6.195	1.0	6.195
H ₂	2.02	5.2	2.574	0.5	1.287
S	32.06	1.0	0.0312	1.0	0.0312
O ₂	32.00	7.0	0.219	-1.0	-0.219
N ₂	28.00	1.4	0.050	0	0
H ₂ O	18.02	2.0	0.111	0	0
ASH	-	<u>9.0</u>	-	-	<u>-</u>
TOTAL		100.0			7.2942

$$\textcircled{\text{e}} \frac{0.79 \text{ mol N}_2}{0.21 \text{ mol O}_2} = 3.762 \frac{\text{mol N}_2}{\text{mol O}_2}$$

& 20% Excess Air

$$0.20 \times 7.2942 \text{ mol O}_2 = 1.459 \text{ mol O}_2 \text{ Excess}$$

$$\text{Total O}_2 = 7.294 \text{ mols} + 1.459 \text{ mols} = 8.753 \text{ mols O}_2$$

$$\text{Total N}_2 = 3.762 \frac{\text{mols N}_2}{\text{mol O}_2} \times 8.753 \text{ mol O}_2 = \underline{32.929 \text{ mols N}_2}$$

$$\text{Total mols dry air} = 41.682 \text{ mols}$$

continued

$$\text{@ } 80^{\circ}\text{F \& } 60\% \text{ R.H.: } 0.0212 \frac{\text{mol H}_2\text{O}}{\text{mol dry air}}$$

(B&W Steam p. 4-A5)

$$\text{H}_2\text{O in Air} = 41.682 \text{ mols dry air} \times 0.0212 \frac{\text{mol H}_2\text{O}}{\text{mol dry air}}$$

$$\text{H}_2\text{O in Air} = 0.884$$

$$\text{Total H}_2\text{O} = \text{H}_2\text{O in Air} + \text{H}_2\text{O in Coal}$$

$$\text{Total H}_2\text{O} = 0.884 \text{ mols} + 0.111 \text{ mols}$$

$$\text{Total H}_2\text{O} = 0.995 \text{ mols H}_2\text{O}$$

$$\text{Total N}_2 = \text{N}_2 \text{ in Air} + \text{N}_2 \text{ in Coal}$$

$$\text{Total N}_2 = 32.929 \text{ mols} + 0.050 \text{ mols}$$

$$\text{Total N}_2 = 32.979 \text{ mols N}_2$$

continued

FLUE GAS

	<u>CO₂</u>	<u>SO₂</u>	<u>O₂</u>	<u>N₂</u>	<u>H₂O</u>	<u>CO</u>	<u>TOTAL</u>
C	6.195	-	-	-	-	--	6.195
H ₂	-	-	-	-	2.574	--	2.574
S	-	0.0312	-	-	-	--	0.0312
O ₂	-	-	1.459	-	-	--	1.459
N ₂	-	-	-	32.979	-	--	32.979
H ₂ O	-	-	-	-	0.995	--	0.995
TOTAL	6.195	0.0312	1.459	32.979	3.569	--	44.233

$$\text{Coal Required} = 8,600 \frac{\text{Btu}}{\text{hr K.W.}} \times 1,000,000 \text{ KW} \times \frac{\#}{13,000 \text{ Btu}}$$

$$\text{Coal Required} = 661,538 \frac{\# \text{ Coal}}{\text{hr}}$$

$$\text{Flue Gas Evolved} = \frac{44.233 \text{ mol flue gas}}{100 \# \text{ coal}} \times 661,538 \frac{\# \text{ coal}}{\text{hr}}$$

$$\text{Flue Gas Evolved} = 292,618 \frac{\text{mol flue gas}}{\text{hr}}$$

TABLE H-96

FLUE GAS PROPERTIES FOR VARIOUS SULFUR BEARING COALS

<u>% S IN COAL</u>	<u>PPM SO₂</u>	<u>MPH</u>	<u>CFS</u> <u>@ 600°F</u>	<u>M. W.</u>	<u>GAS DENSITY</u> <u>@ 600°F</u>
1	705	292,618	62,879	29.60	0.0383
3	2146	288,583	62,012	29.61	0.0383
5	3627	284,567	61,149	29.62	0.0383

APPENDIX I

FLUID BED PROCESS VESSEL SKETCHES

A sample calculation of the minimum fluidization velocity in the fluid bed sorber is presented in Table I-97. Vessel sketches of the major pieces of equipment in the fluid bed process are shown.

TABLE I-97

SAMPLE CALCULATION OF THE MINIMUM FLUIDIZATION VELOCITY

BY THE METHOD OF LEVA, ET. AL. ¹

$$G_{MF} = \frac{688 \cdot D_p^{1.82} \cdot [\rho_f (\rho_s - \rho_f)]^{0.94}}{\mu^{0.88}}$$

where:

G_{MF} = Mass velocity @ minimum fluidization, lb/hr ft²
 D_p = Particle diameter, in. = 0.0359 in.
 ρ_f = Fluid density, lb/ft³ = 0.0409 lb/ft³
 ρ_s = Particle density, lb/ft³ = 70 lb/ft³
 μ = Fluid viscosity, cp = 0.0286 cp
 T = 600°F
 P = 1 psig

$$G_{MF} = \frac{688 \cdot (0.0359)^{1.82} \cdot [0.0409 (70 - 0.0409)]^{0.94}}{(0.0286)^{0.88}}$$

$$G_{MF} = 98.9 \text{ lb/hr ft}^2$$

Since:

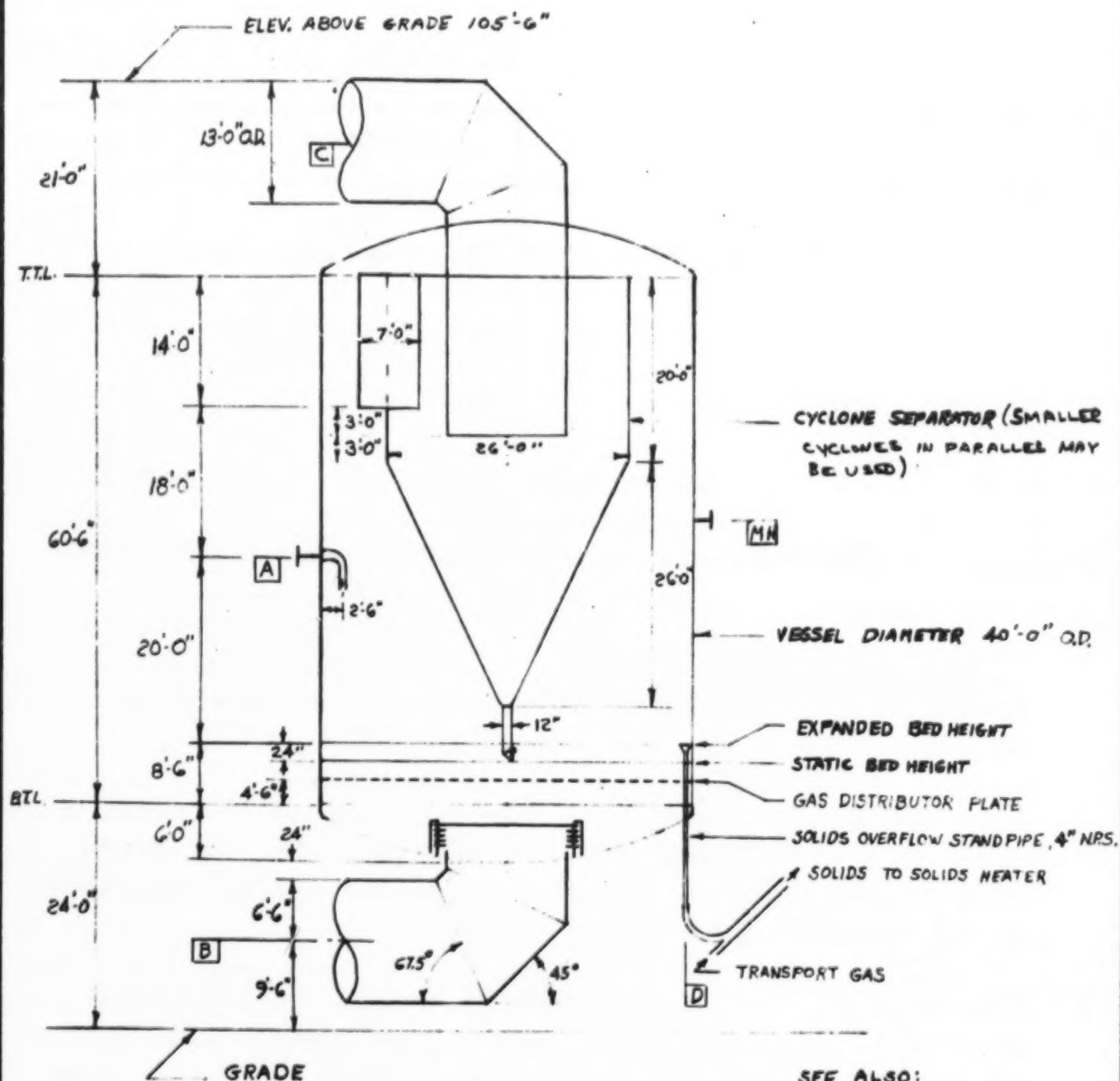
$$u_{MF} = \frac{G_{MF}}{\rho_f \cdot 3600}$$

$$u_{MF} = \frac{98.9}{0.0409 \cdot 3600}$$

$$u_{MF} = 0.671 \frac{\text{ft}}{\text{sec}}$$

1. Leva, M., McGraw-Hill Book Company, Inc., New York, 1959

FIG. I-99



					SCALE: NTS	THE M. W. KELLOGG CO.		
					DRAWN: GMD			
					CHECKED:			
					APPROVED:			
					DATED: 3-31-69	FLUID BED SORBER		
					ISSUED FOR FABRICATION			
NO.	DESCRIPTION	DATE	BY	CHK.	ISSUED FOR CONSTRUCTION	D-10-1	6045	AA-FB-3-A1
REVISIONS						CLASS. & ITEM	JOB NO.	DRAWING NO.

REPLACES NO. 107H 50000

-I447-

A
94X11

FOR NAPCA

LOCATION

SUBJECT FLUID BED SORBERS D-1a-jJOB No. 6045PAGE AA-FB-3-A2DATE 3-31-69BY GMD

TABLE OF CONNECTIONS

SYM.	SIZE	SERVICE	REMARKS
A	6"	DILUTE PHASE SOLIDS INLET	FROM D-2 SEE NOTE 4
B	13'-0"	GAS INLET	SEE NOTES 5 & 6
C	13'-0"	GAS OUTLET	SEE NOTE 5
D	4"	DENSE PHASE SOLIDS EXIT	TO D-3 SEE NOTE 7
M-H		MAN HOLE	NUMBER & SIZE BY VESSEL ANAL.

NOTES:

1. VESSEL SHELL DIAMETER 40'-0" LINED W/ 6" INSULATION AS PER PIPING SPEC.
2. GAS DISTRIBUTOR PLATE IS A FLAT PLATE W/ 34,700 HOLES @ $\frac{1}{2}$ " DIA. & $2\frac{3}{8}$ " CENTER - CENTER SPACING. MAXIMUM STATIC LOAD ON THE PLATE IS 170,000 LBS. GAS ΔP ACROSS THE PLATE IS 4.9 IN. H₂O. SUPPORT AS REQ'D.
3. CYCLONE SIZES SHOWN ARE APPROXIMATE AND TO BE CONFIRMED BY VENDOR. CYCLONE IS TO BE LINED W/ AN EROSION RESISTANT MAT'L. INLET GAS VELOCITY 60' / SEC, 5920 ACFS. SOLIDS LOADING 113 GRAINS / ft². DIP LEG DIA. IS 12" W/ FLAPPER TYPE OR EQUIVALENT DISCHARGE, MINIMUM DIP LEG DISCHARGE 1' BELOW EXPANDED BED HT. MAX. CYCLONE ΔP = 6 IN. H₂O.
4. SHELL NOZZLE A, 6" INTERNAL PIPING 12", PROVIDE 90° LR ELBOW TO DIRECT INLET SOLIDS FLOW TO BED. NOZZLE ORIENTATION 180° FROM NOZZLE D.

(CONT.)

FIG. I-99
(CONT'D)FOR NAPCA

LOCATION

SUBJECT FLUID BED SORBERS D-12-j
 JOB No. 6045
 PAGE AA-FB-3-43
 DATE 3-31-69
 BY GMP

NOTES (CONT.)

5. NOZZLES B & C EXTENDED TO SHOW PIPING ELEVATIONS. MITER ANGLES SHOWN ARE TYPICAL. ALL NOZZLE PARTS AND PIPING EXTERNAL TO VESSEL ARE TO BE LINED W/ INSULATION AS PER THE PIPING SPEC. INTERNAL NOZZLE CONNECTIONS NEED NOT BE INSULATED.
6. NOZZLE B HAS A BAFFLE TYPE INLET DISTRIBUTOR. SEE DWG. AA-FB-3-A4. SUPPORT AS REQ'D.
7. NOZZLE D IS EXTENDED AND CONNECTED BY MEANS OF A PIPE BEND AND Y TYPE JUNCTION TO THE DILUTE PHASE TRANSFER LINE TO THE SOLIDS HEATER. THE INTERNAL ELEVATION OF THE NOZZLE IS SET BY THE EXPANDED BED HT. AT THE Φ OF THE INTERNAL STAND PIPE IS A 60° INCLUDED ANGLE CONE 1'-0" DIA @ BASE. THE SOLIDS IN THE STAND PIPE WILL BE FLUIDIZED WITH AN EXTERNAL MEDIUM WHOSE COMPOSITION & FLOW WILL BE SPECIFIED LATER.

DESIGN DATA
 INLET PRESSURE : 43" H₂O
 OUTLET PRESSURE : 13" H₂O

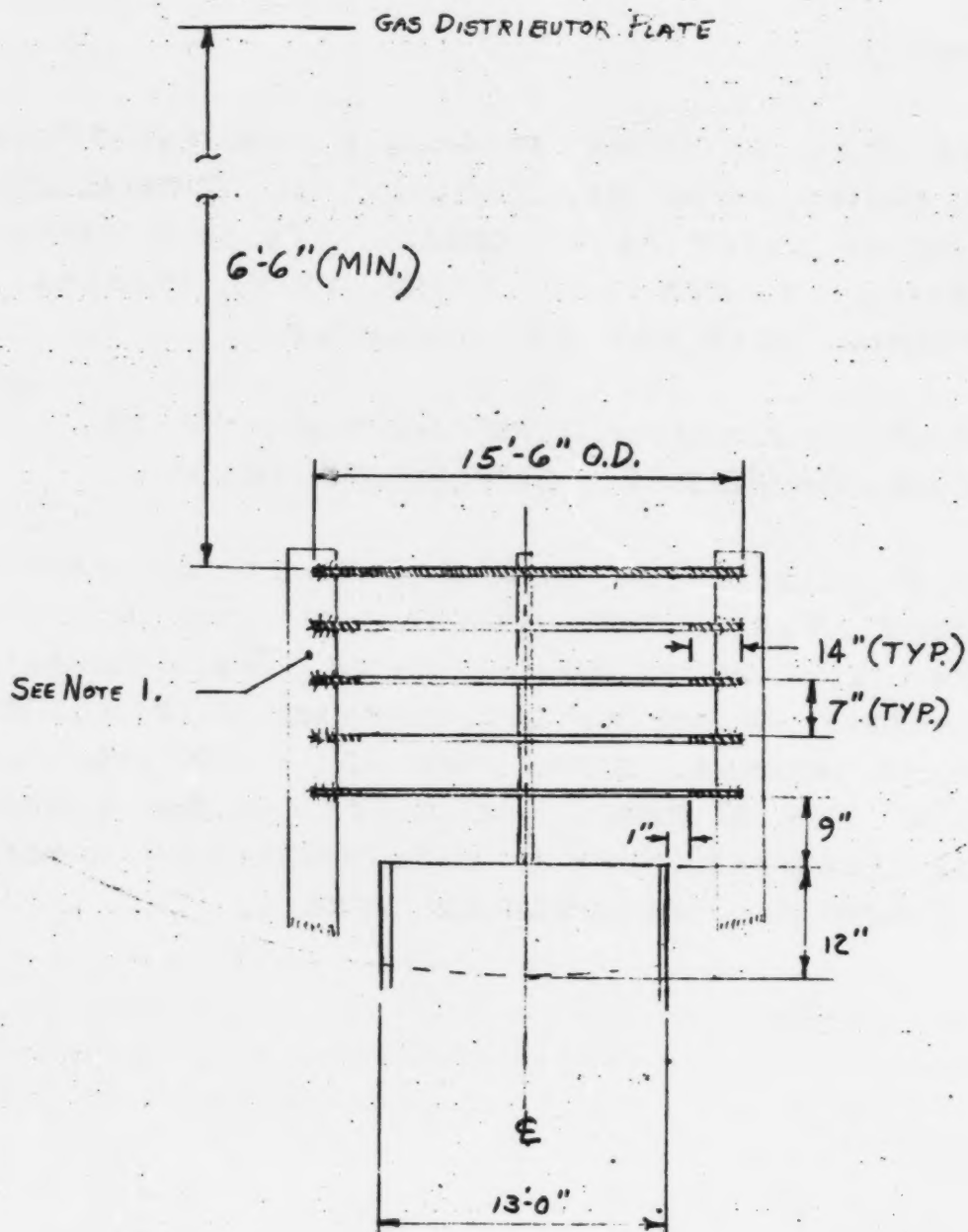
TEMPERATURE: 600°F

CYCLONE ΔP : 6 IN H₂O

WE OF BED (MAX.) 170,000 lbs

GRID ΔP : 49 IN H₂OINLET ΔP : 0.6 IN H₂O

FIG. I-99
(CONT'D)



NOTES:

1. NUMBER, SIZE AND PLACEMENT OF VANES TO BE SPECIFIED BY VESSEL MECHANICAL. AT LEAST 4 VANES ARE REQUIRED.

					SCALE: <i>NTS</i>	THE M. W. KELLOGG CO.			
					DRAWN: <i>GMD</i>				
					CHECKED:				
					APPROVED:				
					DATED: <i>3-31-69</i>	INLET BAFFLE DISTRIBUTOR			
					ISSUED FOR FABRICATION				
NO.	DESCRIPTION	DATE	BY	CHK.	ISSUED FOR CONSTRUCTION	D-1a-j		6045	AA-FB-3-A4
REVISIONS						CLASS & ITEM	AREA	JOB NO.	DRAWING NO.

DEFIANCE NO. 167H 88000



FIGURE I-100

BY: GMD
REV. NO. _____ BY: _____
APPROVED: _____ DATED: 4-17-69

VESSEL SKETCH
FOR PROCESS INFORMATION ONLY
REGENERATOR

JOB NO: 6045
EST. NO. _____
ITEM NO: D-2a#b

R & ED 5 PROCESS VESS 10-67

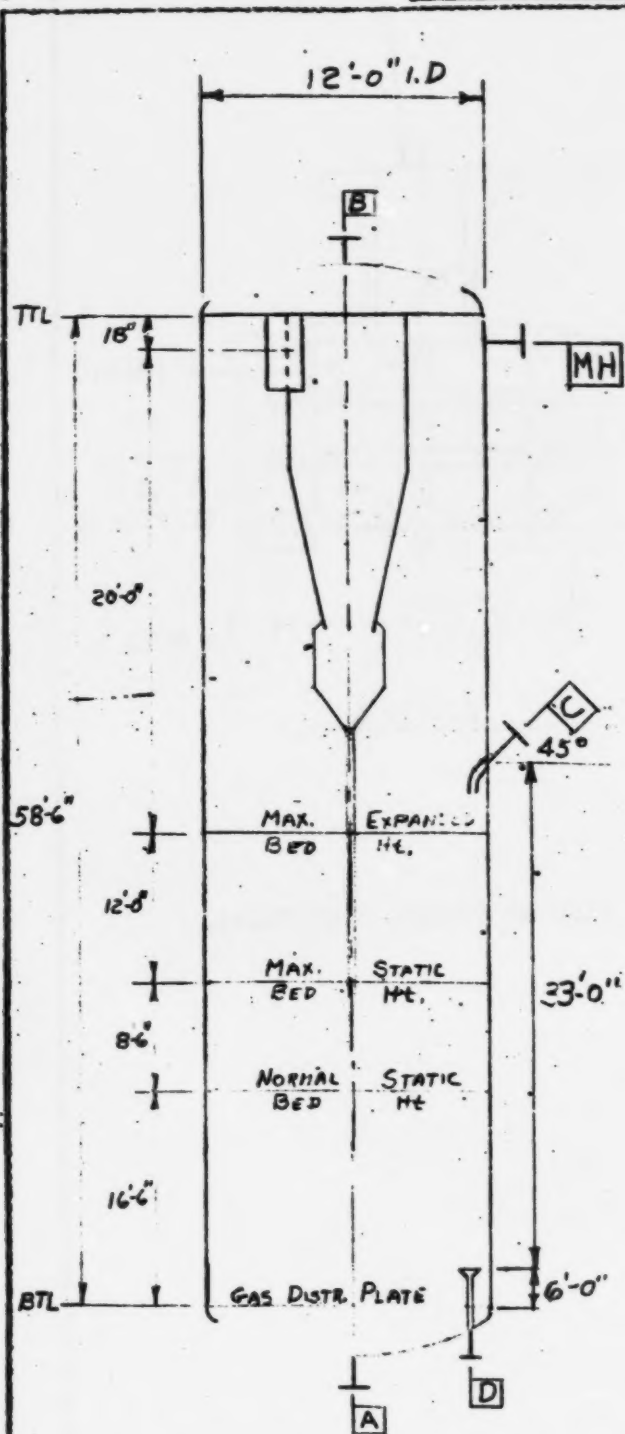


TABLE OF PROCESS CONNECTIONS

SYM.	SIZE	SERVICE	REMARKS
A	20"	GAS INLET	SEE NOTE 1 B
B	30"	GAS OUTLET	SEE NOTE 5
C	10"	SOLIDS INLET	SEE NOTE 6
D	10"	SOLIDS OUTLET	SEE NOTE 7
MH		MANHOLES	AS REQ'D.

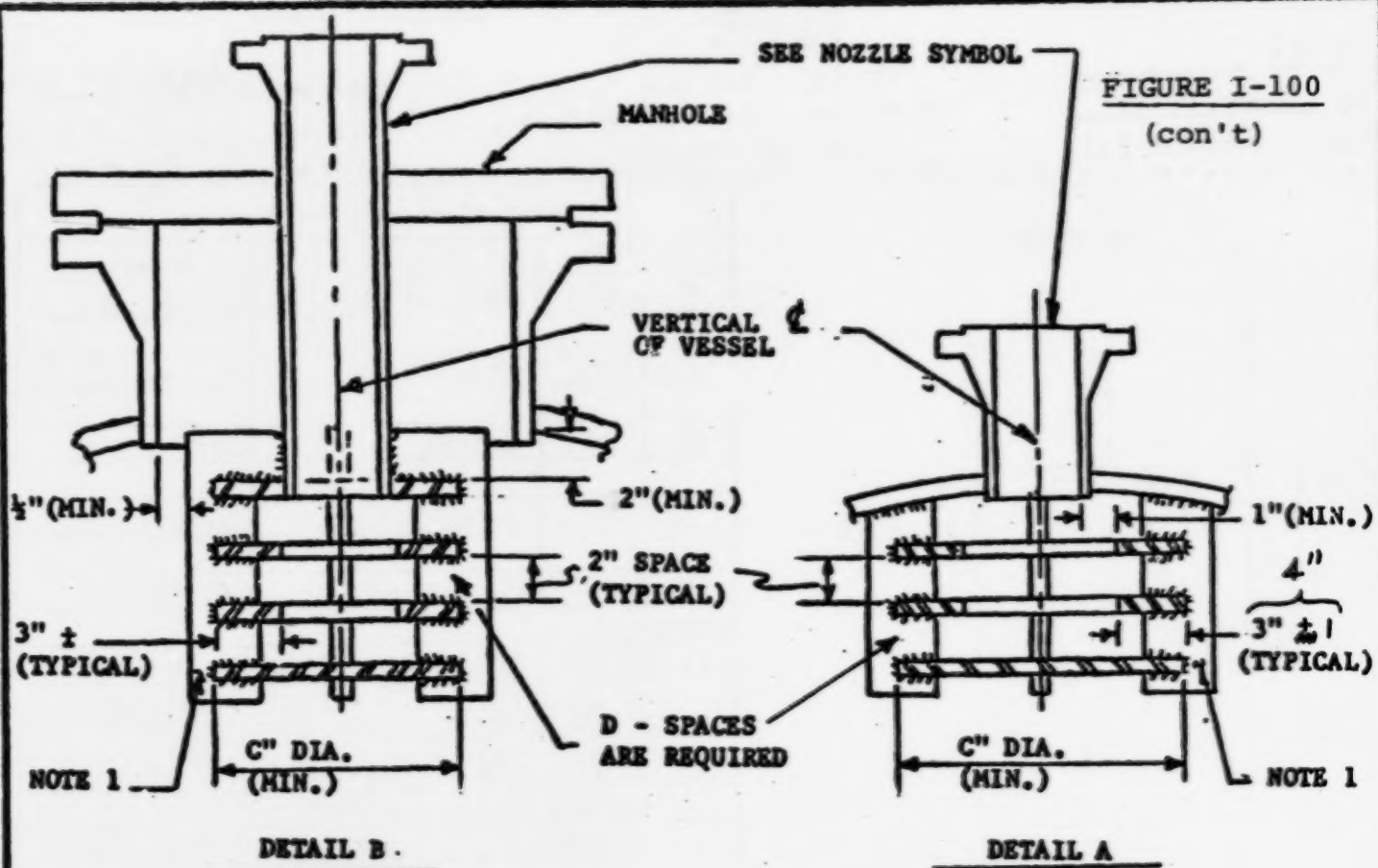
NOTES:

1. VESSEL MECHANICAL TO SPECIFY MATERIALS OF CONSTRUCTION. SEE THE MATERIALS OF CONSTRUCTION SPECIFICATION AND/OR DESIGN DATA SHEETS ISSUED FOR THIS JOB FOR CORROSION ALLOWANCE, ETC.
2. MANHOLE SIZES (IF STATED) CORRESPOND TO REQUIREMENTS. IF NOT STATED, VESSEL MECHANICAL TO SPECIFY MANHOLE SIZES REQUIRED BY JOB SPECIFICATIONS AND/OR DESIGN DATA SHEETS.
3. VESSEL SHELL 13'-0" LINED W/ 6" GUNITED CASTABLE INSULATION
4. GAS DISTRIBUTOR PLATE IS A FLAT PLATE W/ 860 HOLES @ 1/2" P AND 4" C-C SPACING. MAXIMUM STATIC LOAD ON PLATE IS 128,000#
5. GAS ΔP ACROSS PLATE IS 0.22 PSI MAX.
6. CYCLONE DU CONE #480-SCDM OR EQUIV. LINED W/ EROSION RESISTANT MAT'L. DIP LEG W/ FLAPPER TYPE DISCHARGE 1'-0" BELOW MAX STATIC BED HT.
7. SHELL NOZZLE C IS 45° HILLSIDE. INTERNAL PIPING 10" 45° LRE
8. SHELL NOZZLE D CONNECTS TO 10" INTERNAL STAND PIPE W/ 2'-0" CONE TOP. 5 REQ'D.
9. NOZZLE A HAS A BAFFLE TYPE INTERNAL DISTRIBUTOR. SEE DWG AA-FB-A2
- 9 ONE VESSEL REQ'D PER TRAIN

DWG. AA-FB-5-A1

PROCESS DATA

WORKING PRESSURE	25 PSIG [DESIGN]	PSIG	REGENERATOR INLET BAFFLE	AA-FB-5-A2
WORKING TEMPERATURE	1400 °F	°F	TITLE	DWG NO.
PRESSURE DROP THROUGH INTERNALS		PS.	-I451-	REFERENCE DRAWINGS



NOTES

1. NUMBER, SIZE AND PLACEMENT OF VANES TO BE SPECIFIED BY VESSEL MECHANICAL. AT LEAST 4 VANES ARE REQUIRED.

TABLE OF DIMENSIONS

NOZZLE SYMBOL	DETAIL	C	D
A	A	28"	3

				SCALE: NTS		THE M. W. KELLOGG COMPANY a division of PULLMAN INCORPORATED	
				DRAWN: GMD		REGENERATOR INLET BAFFLE	
NO.	REVISION DESCRIPTION	DATE	BY	CHK.	APPROVED:	6045	AA-FB-5-A2
ISSUED FOR FABRICATION		ISSUED FOR CONSTRUCTION		DATED: 4-17-69		CLASS	AREA
						JOB NO.	DRAWING NO.

I452-



FIGURE I-101

FOR NAPCA
LOCATION Fluid Bed Design
SUBJECT Fluid Bed Design

JOB NO. 6045
PAGE 4/18/69
DATE 4/18/69
BY

D-3 a & b - Fluid Bed Solids Heater (1 REQ'D/TRAIN - TOTAL OF 2)

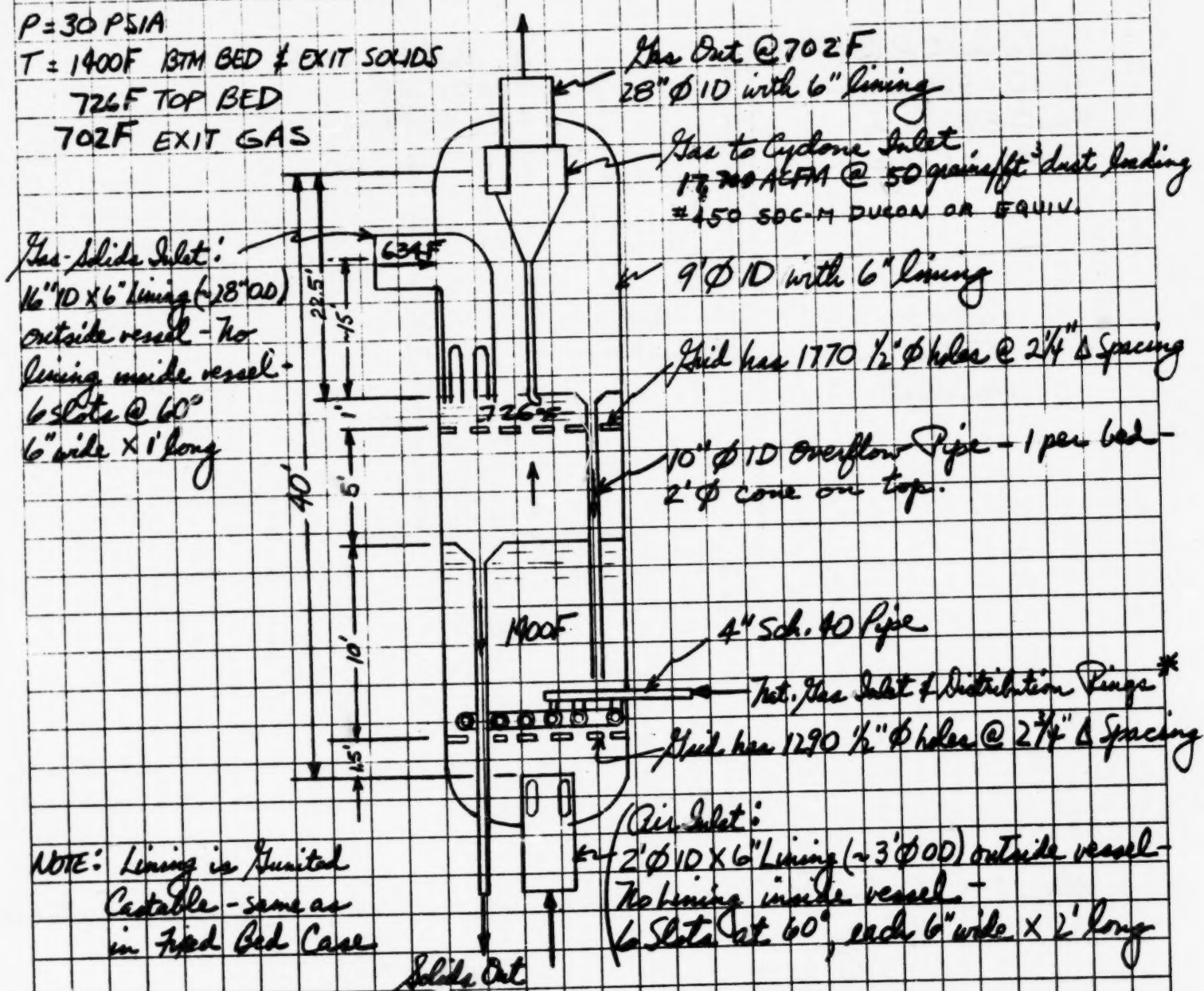
Duty: To heat 189,900 lbs/hr solids from 634F → 1400F in two stages: 1-stage direct combustion of natural gas in bed at 1400F; 1-stage heat exchange between exit gas and entering solids.

P = 30 PSIA

T = 1400F BTM BED & EXIT SOLIDS

726F TOP BED

702F EXIT GAS



* 3 Distribution Rings Required:

1. 4" Pipe, 9' ϕ 110 - $\frac{1}{4}$ " ϕ holes
2. 3" Pipe, 5' 4" ϕ 65 - $\frac{1}{4}$ " ϕ holes
3. 1 1/2" Pipe, 1' 6" ϕ , 20 - $\frac{1}{4}$ " ϕ holes

FOR **NAPCA**
LOCATION
SUBJECT **Fluid Bed Design**

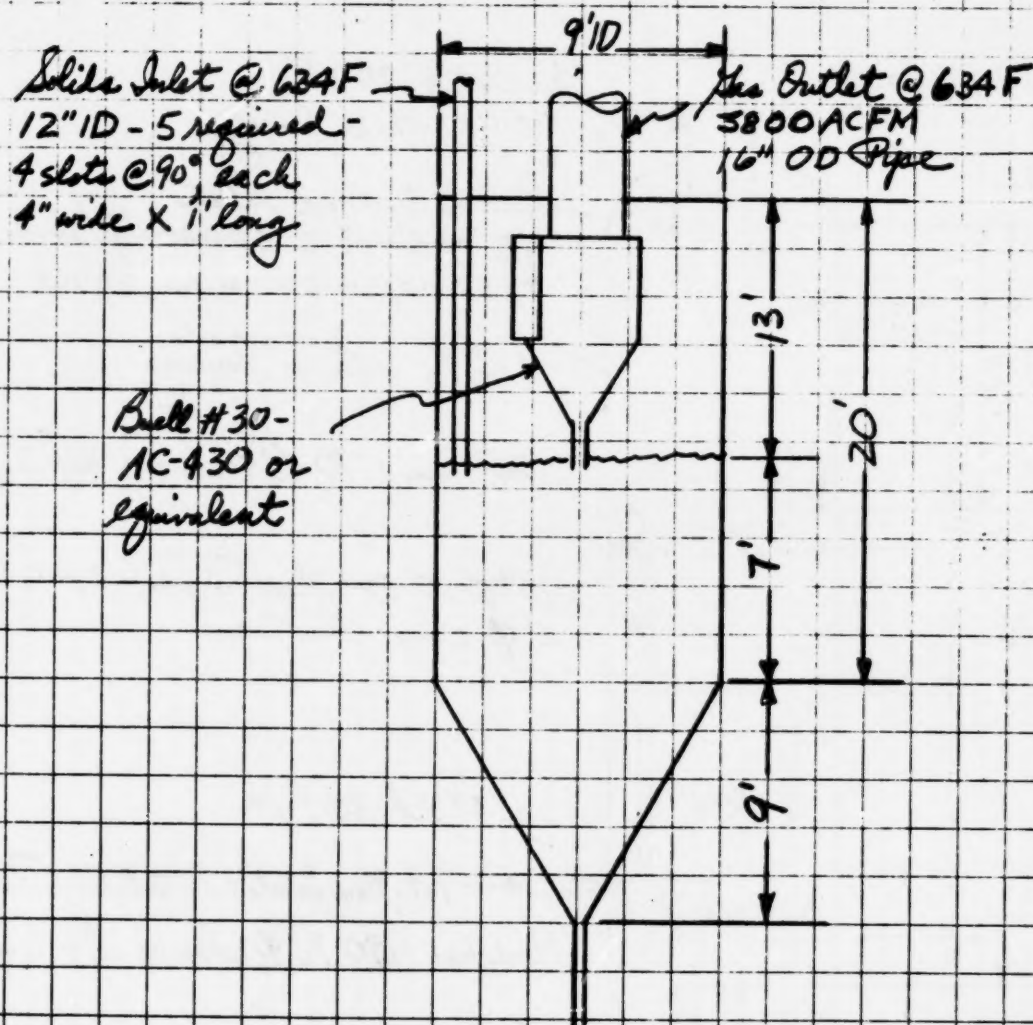


FIGURE I-102

JOB NO. **6045**
PAGE
DATE **4/16/69**
BY

L-1 a+b - Gas-Solids Separator

(1 REQ'D/TRAIN - TOTAL OF 2)



- NOTES:
- Carbon Steel construction with 6" thickness Hunted Castable Lining.
 - Maximum Solids Hold-Up = 44,500 lbs
 - $T = 634F$
 $P_{DESIGN} = 1 PSIG$

APPENDIX J

FIXED BED SORBER DESIGNS

Table J-98 shows sorber dimensions for various sorption times based on the rectangular sorption panel design shown in Figure J-111. These are included to illustrate the variation in bed thickness, sorbent volume (which can be calculated from the data shown), and pressure drop as sorption time changes. Sorbent volume, bed thickness, and pressure drop are the same for other panel configurations (e.g., cylindrical).

Table J-99 summarizes the results of the search for a vendor to supply the large diameter (20 feet) valves needed in the fixed bed design.

Two different types of gas-solids contactors are shown in Figures J-108 and J-109. These have possible applications in the fixed bed design but were not evaluated in the present study since no large economic savings or other advantages were apparent.

Figures J-110 through J-119 show details of the rectangular sorber design which was first considered for the fixed bed process. It was later abandoned in favor of the cylindrical design shown in Figures J-120 and J-121 but is included here since it may have application in some other process where the temperature level and variation is less than for the alkalized alumina process.

TABLE J-98

FIXED-BED SORBER DIMENSIONS

T	ΔP	A	B	C	D
24	30	12"	15"	21-1/2"	18-1/2"
24	2	4"	7"	8"	5"
12	30	18"	21"	16"	13"
12	2	5"	8"	6-1/2"	3-1/2"
6	30	21"	2'-0"	12"	9"
6	2	7"	10"	5-1/2"	2-1/2"
4	30	2'-1"	2'-4"	10"	7"
4	2	8"	11"	5"	2"

A = Minimum required distance between sorber panels (may be increased if necessary for mechanical design reasons).

B = Width of sorber panel covers.

C = Width of sorber panels.

D = Sorbent bed thickness.

T = Sorption stream time, hours.

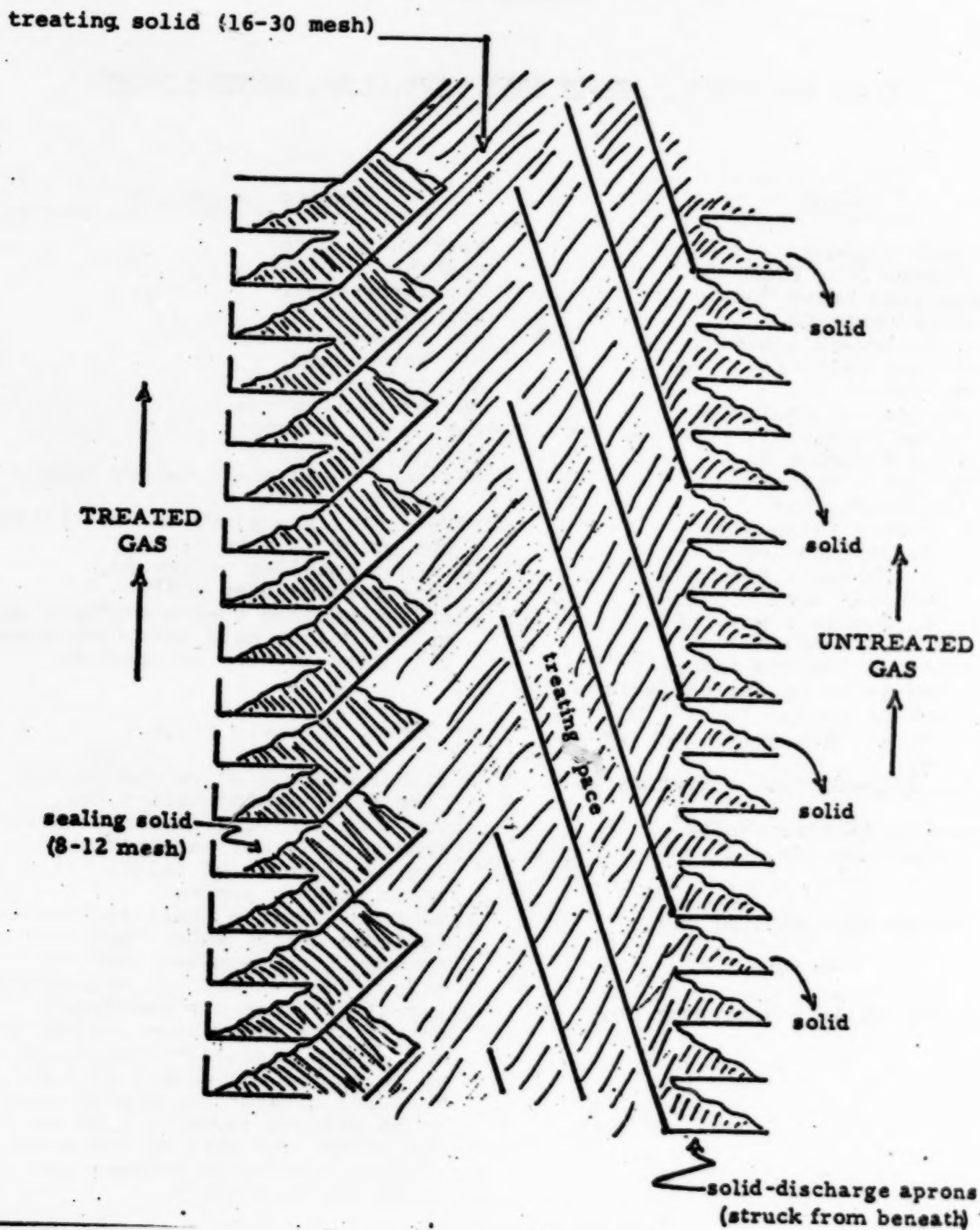
ΔP = Pressure drop through sorber panel, inches of water.

TABLE J-99

FIXED BED SCHEME - VENDOR SEARCH FOR 20 FT. DIAMETER VALVES

<u>VENDOR</u>	<u>RESULTS OF CONTACT</u>
Crane Company	Nothing to offer.
Chapman Div. Crane Co.	Nothing to offer.
Keystone Valve Corp.	Not interested.
Henry Pratt Co.	Not interested.
W. G. Rovang & Assoc.	Not interested.
Darling Valve Co.	Not interested.
Wm. Powell Co.	Not interested.
Continental Equip. Co.	Beyond their scope.
Valcon Equip. Co.	Beyond their scope.
Fluid Dynamics Inc.	Beyond their scope.
Babcock & Wilcox Equipment Div.	Will not build their damper type valves for others.
S. Morgan Smith Div. of Allis-Chalmers	Have design & production capabilities but price is very high.
W. S. Rockwell Div. of Rockwell Mfg.	Will not consider valves for temperatures over 900°F.
W. S. Rockwell Div. of Rockwell Mfg. (When we lowered temp.) Requested copies of design MWK developed for 14' x 16' louver vane valve some years ago.	Withdrawing from specialty field and will consider only that work which will lead to mass production.
Sun Shipbuilding & Drydock Co.	No longer in their files.
Golden Anderson Valve Specialty Co.	Will build anything we design and take full responsibility for. Think they can provide these valves economically but have not sub- mitted anything of value, but are currently active.
Hammel-Dahl Div. of ITT	Expect to submit a realistic butter- fly type design which they will have built by someone like Sun Ship. But H-D will be responsible.
Grove Valve & Regulator Co.	Original offering was completely unrealistic. They have redesigned and have a retracted disc valve which can be reasonably priced. The preliminary design will have to be refined to water cool or otherwise take care of the temp- erature difference between the valve and duct walls.

FIGURE J-103
COUNTER-CURRENT GAS-SOLID CONTACTING PANEL
Arthur M. Squires



NOT REPRODUCIBLE

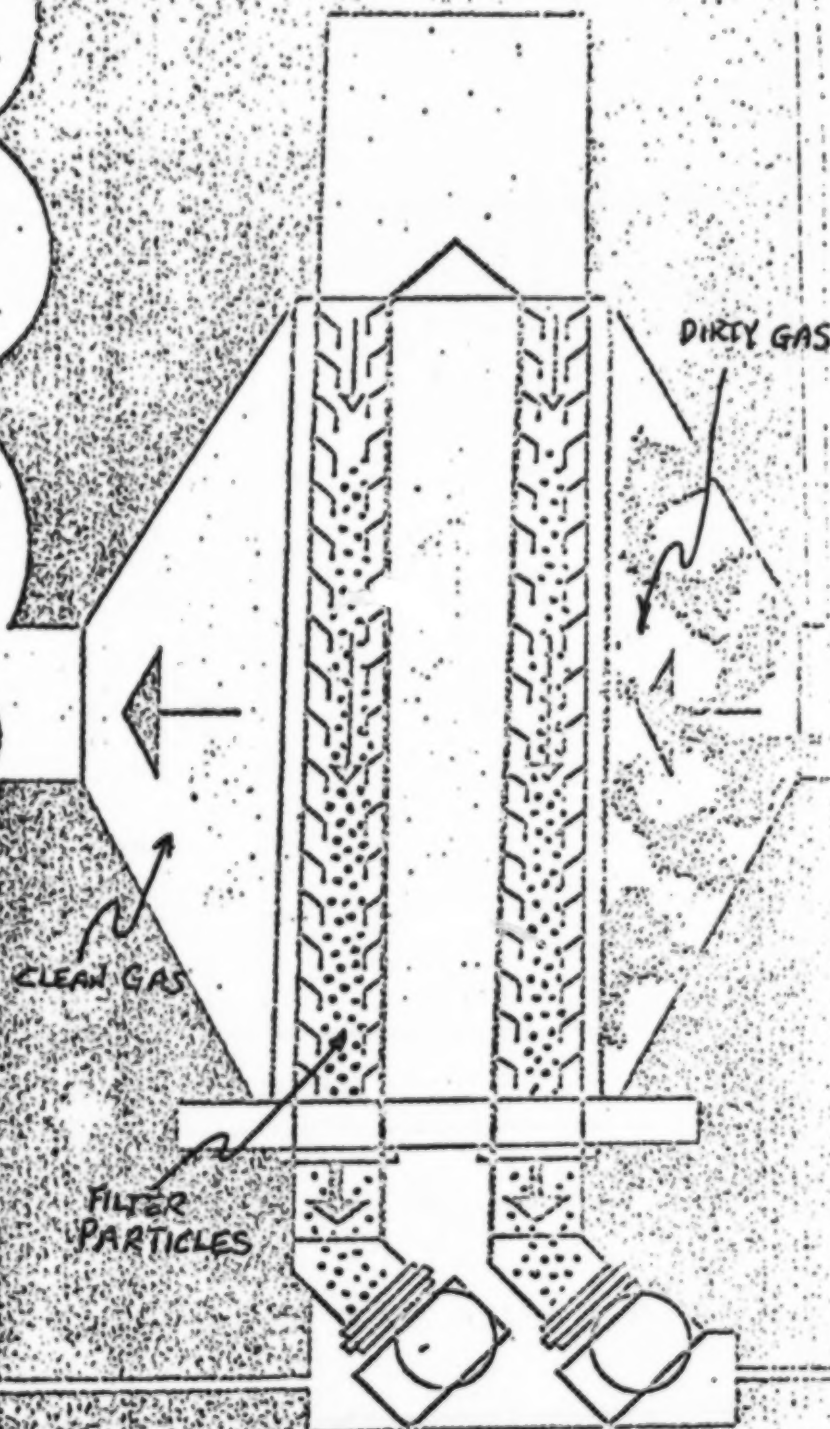
FIGURE J-104

The
DORFAN

Impingo
Filter

FOR CLEANING

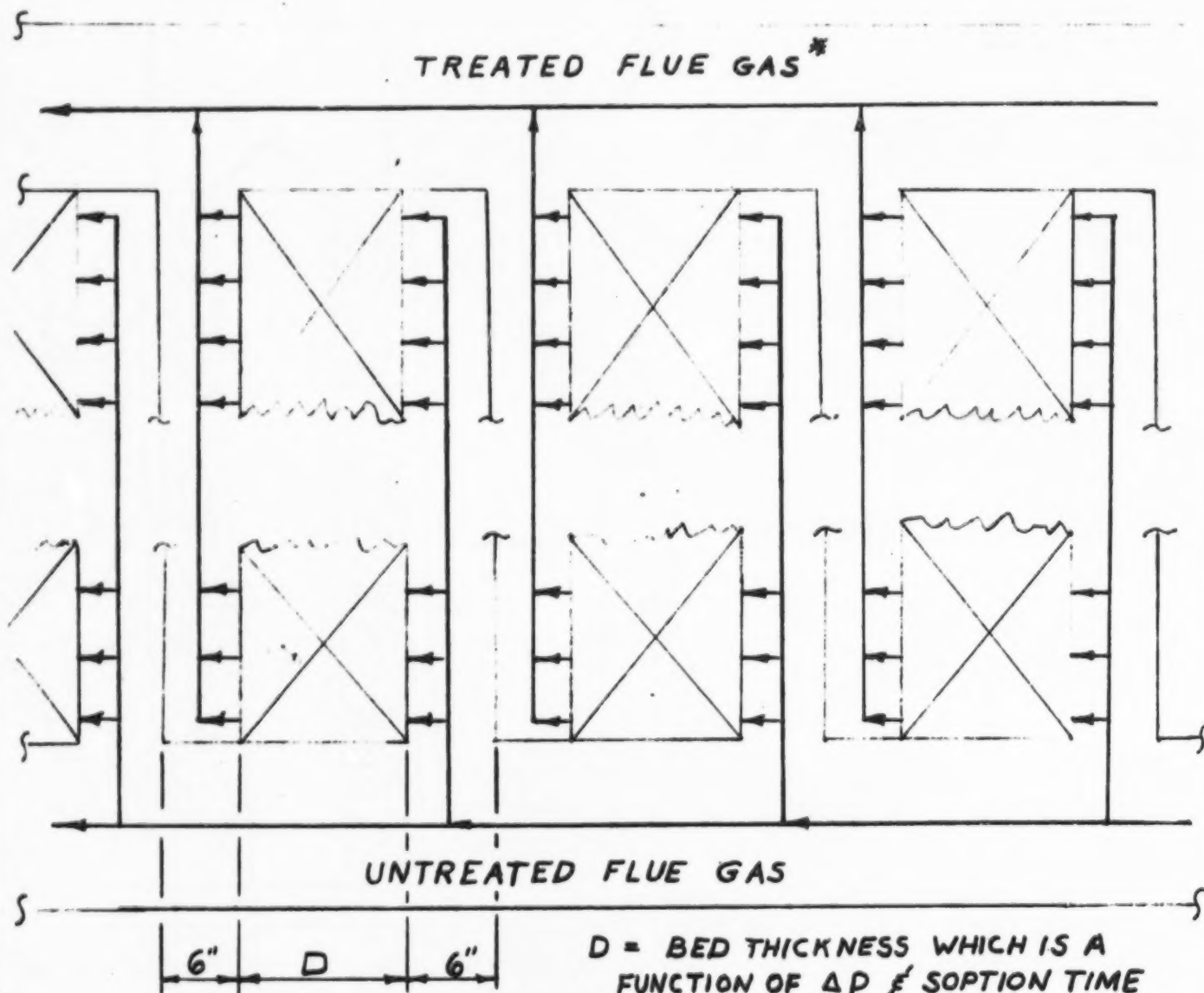
Hot, wet and
corrosive
GASES-AIR



MECHANICAL INDUSTRIES, INCORPORATED

FIGURE J-105

CROSS-SECTIONAL VIEW OF SORBER FLOW



* FLUE GAS AFTER 90% OF THE INLET SO_2 IS REMOVED

<table border="1"> <tr> <td>NO.</td> <td>DESCRIPTION</td> <td>DATE</td> <td>BY</td> <td>CHK.</td> </tr> <tr> <td colspan="5">REVISIONS</td> </tr> </table>					NO.	DESCRIPTION	DATE	BY	CHK.	REVISIONS					SCALE: <i>NTS.</i>	THE M. W. KELLOGG CO.		
					NO.	DESCRIPTION	DATE	BY	CHK.									
					REVISIONS													
					DRAWN: <i>GMD</i>													
					CHECKED:													
APPROVED:																		
DATED: <i>11-25-68</i>					SORBER FLOW PATTERN													
ISSUED FOR FABRICATION																		
ISSUED FOR CONSTRUCTION																		
					CLASS & ITEM	AREA	JOB NO. <i>6045</i>	DRAWING NO.										

A
8 1/2 X 11

DEPLANCE NO. 167H 00000

-J460-

FIGURE J-106

SORBER PANEL

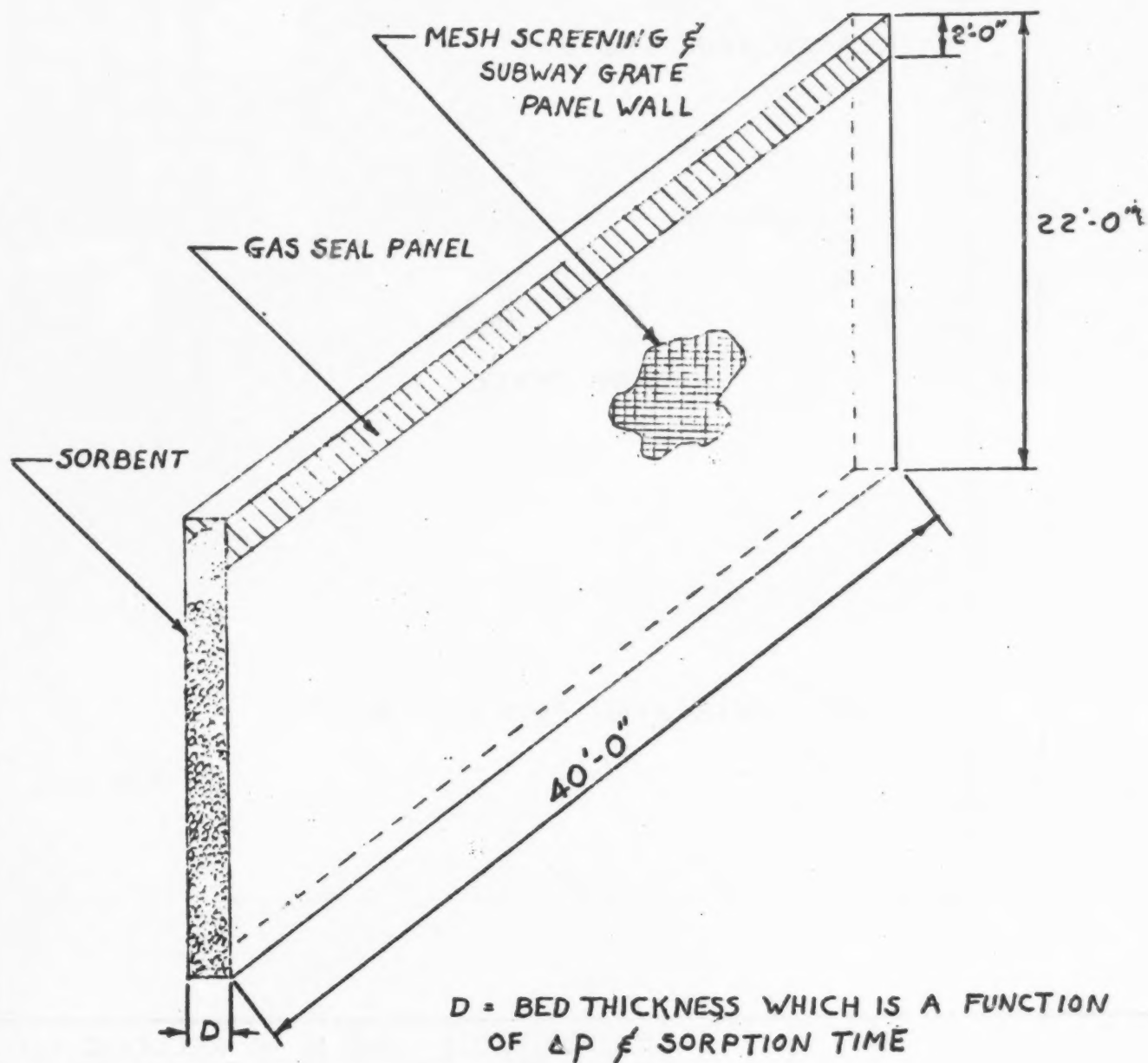
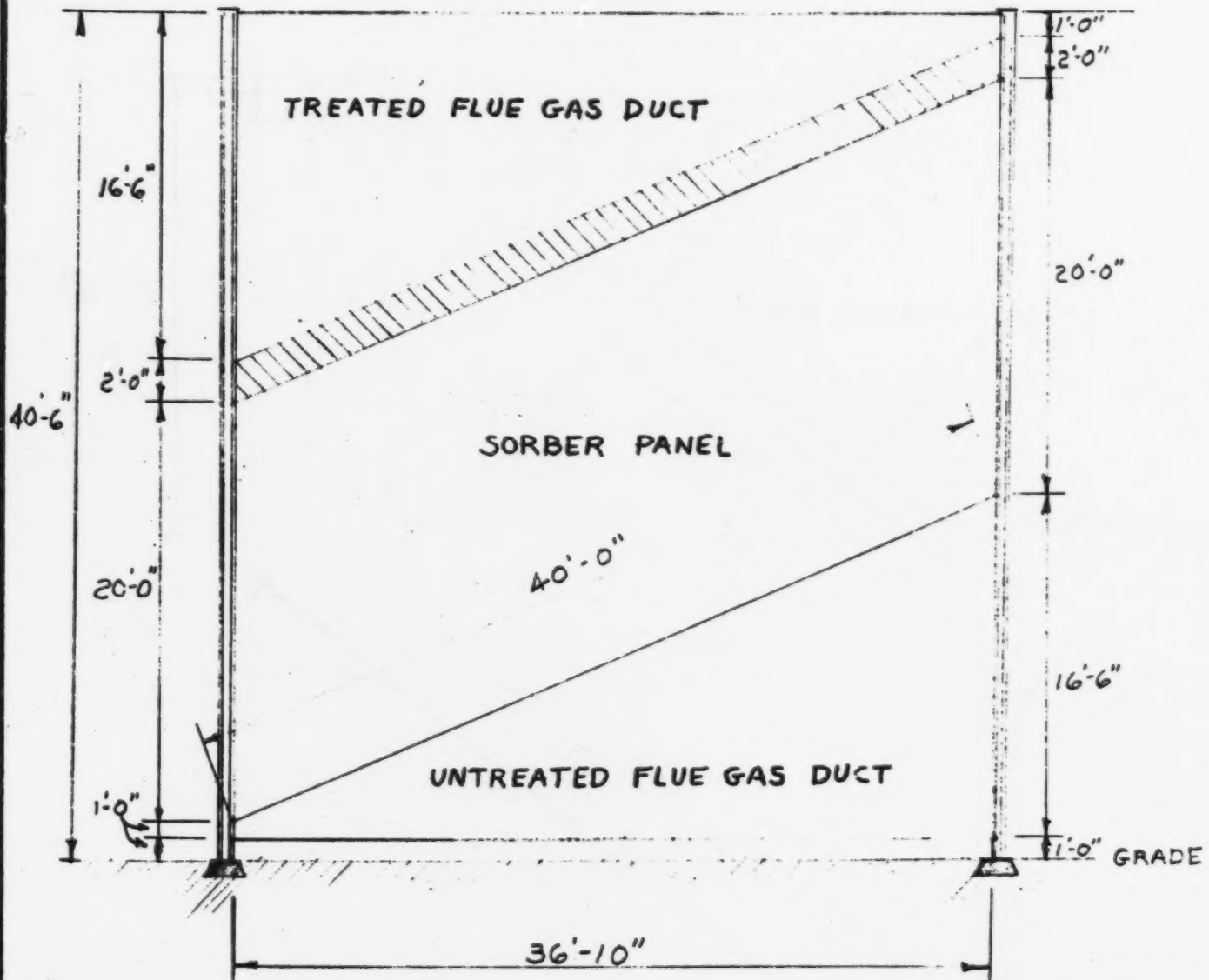


FIGURE J-107

FRONT VIEW OF SORBER



				SCALE: $\frac{1}{8}$ "-1'-0"		THE M. W. KELLOGG CO.			
				DRAWN: GMD					
				CHECKED:					
				APPROVED:					
				DATED: 11-25-68		SORBER FRONT VIEW			
				ISSUED FOR FABRICATION					
NO.	DESCRIPTION	DATE	BY	CHK.	ISSUED FOR CONSTRUCTION	CLASS & ITEM	AREA	JOB NO.	DRAWING NO.
REVISIONS									

DEPIANCE NO. 107H 00000

-J462-

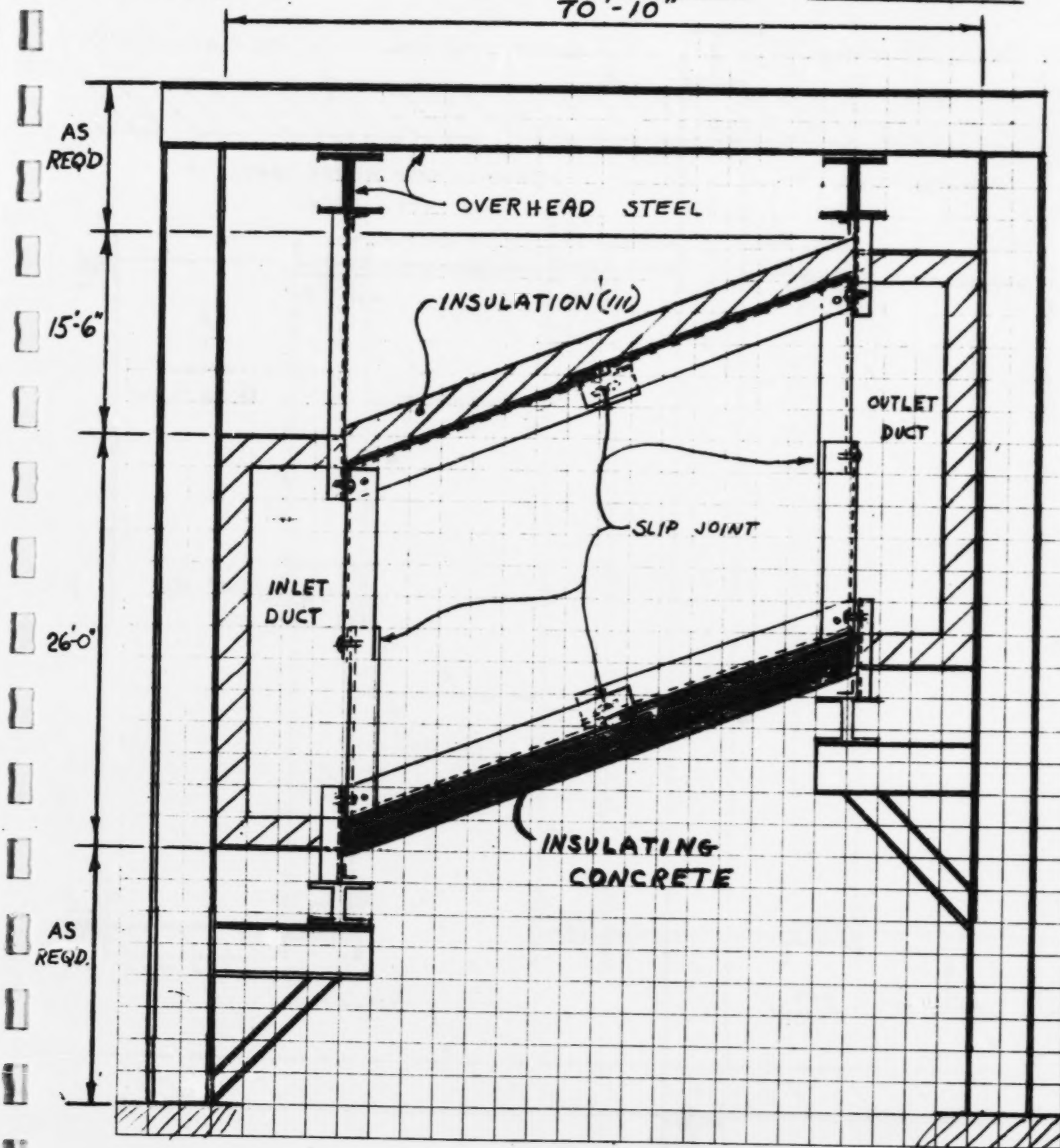
A

04X11

FIXED BED

FIGURE J-108
70'-10"

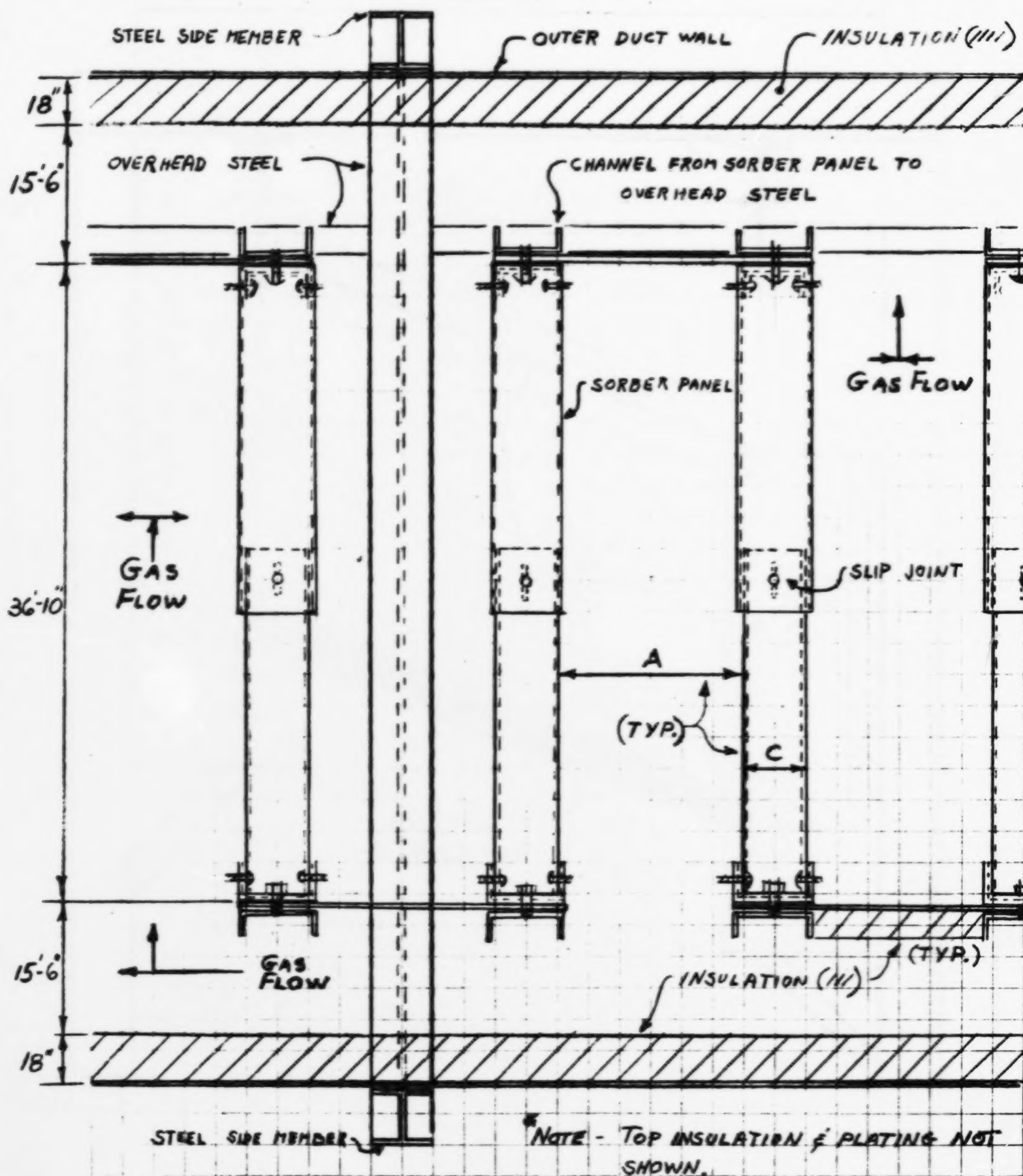
SORBER FRONT VIEW



FIXED BED

SORBER PLAN VIEW

FIGURE J-109

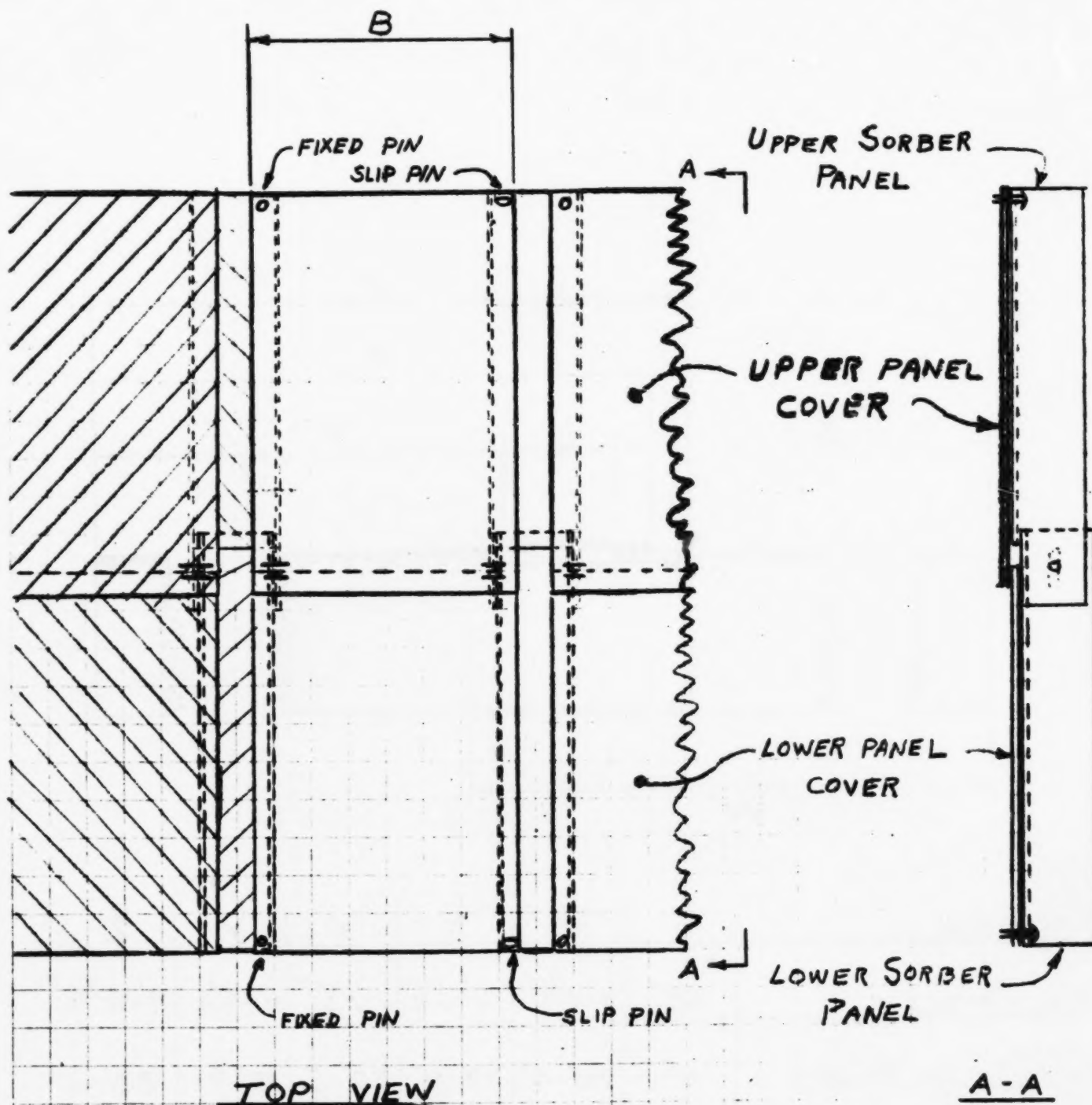


FIXED BED

FIGURE J-110

TOP & BOTTOM SORBER PANEL COVER

DETAIL

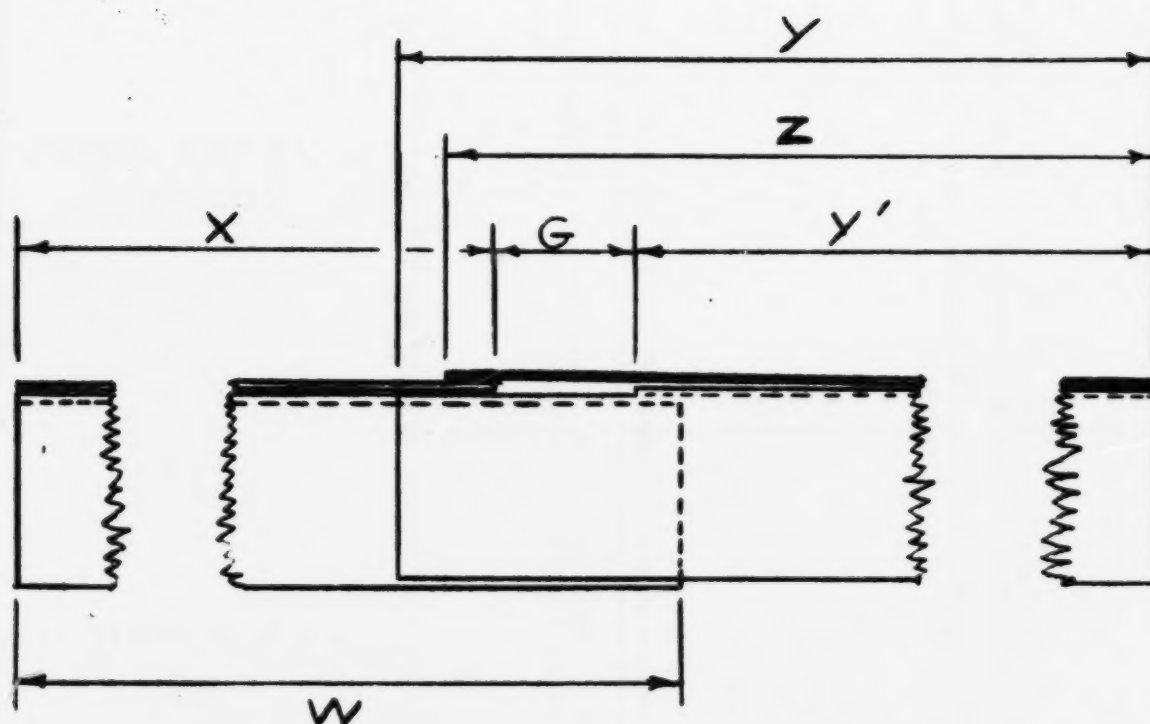


NOTE - INSULATION NOT SHOWN

FIXED BED

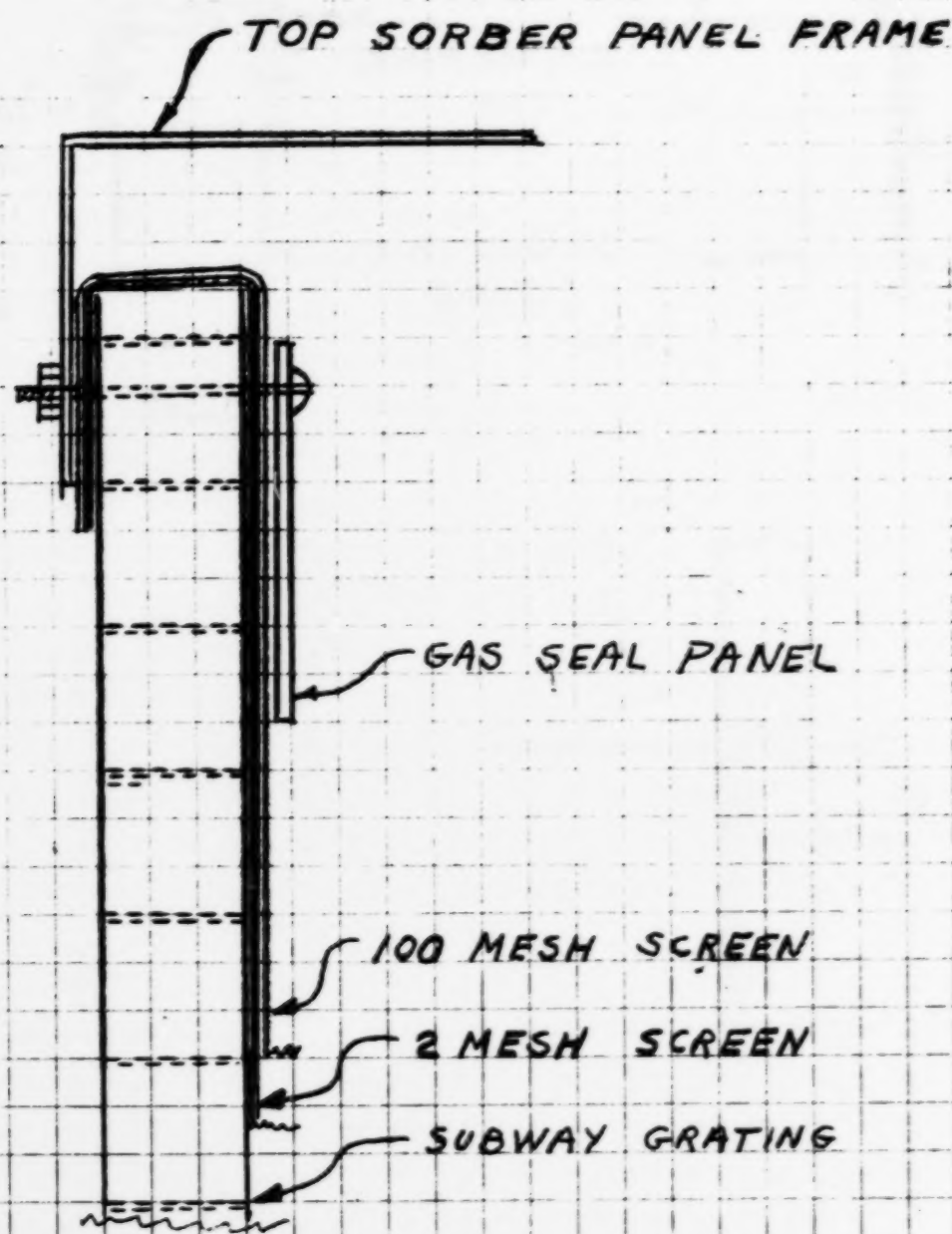
FIGURE J-111

SORBER PANEL
FRAME DIMENSIONS



DIMENSION	G	W	X	Y	Y'	Z
SIDE PANELS	3½"	11'-8¾"	11'-4¼"	11'-9¾"	11'-4¼"	11'-8¾"
TOP & BOTTOM PANELS	6"	20'-4"	19'-9"	20'-5"	19'-9"	20'-4"

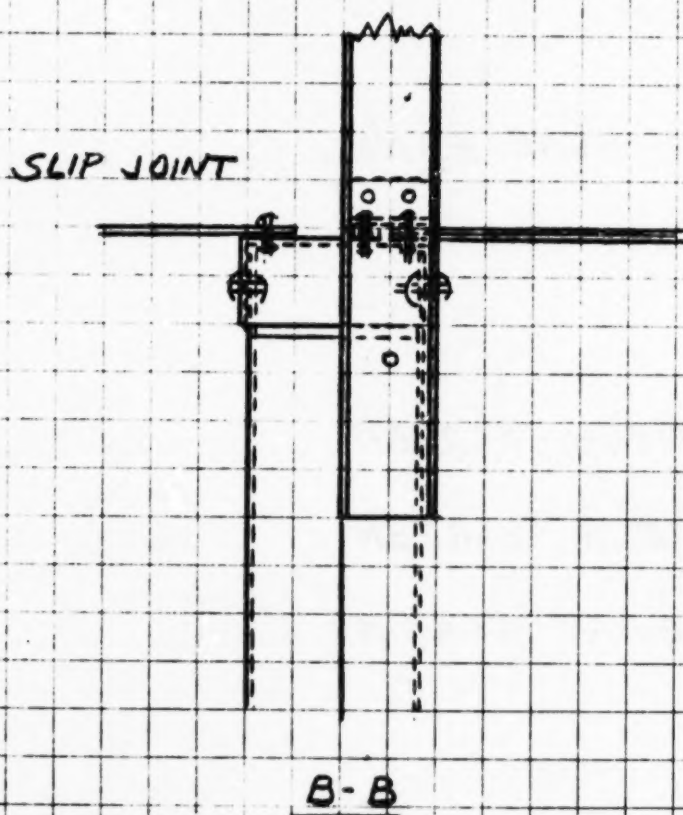
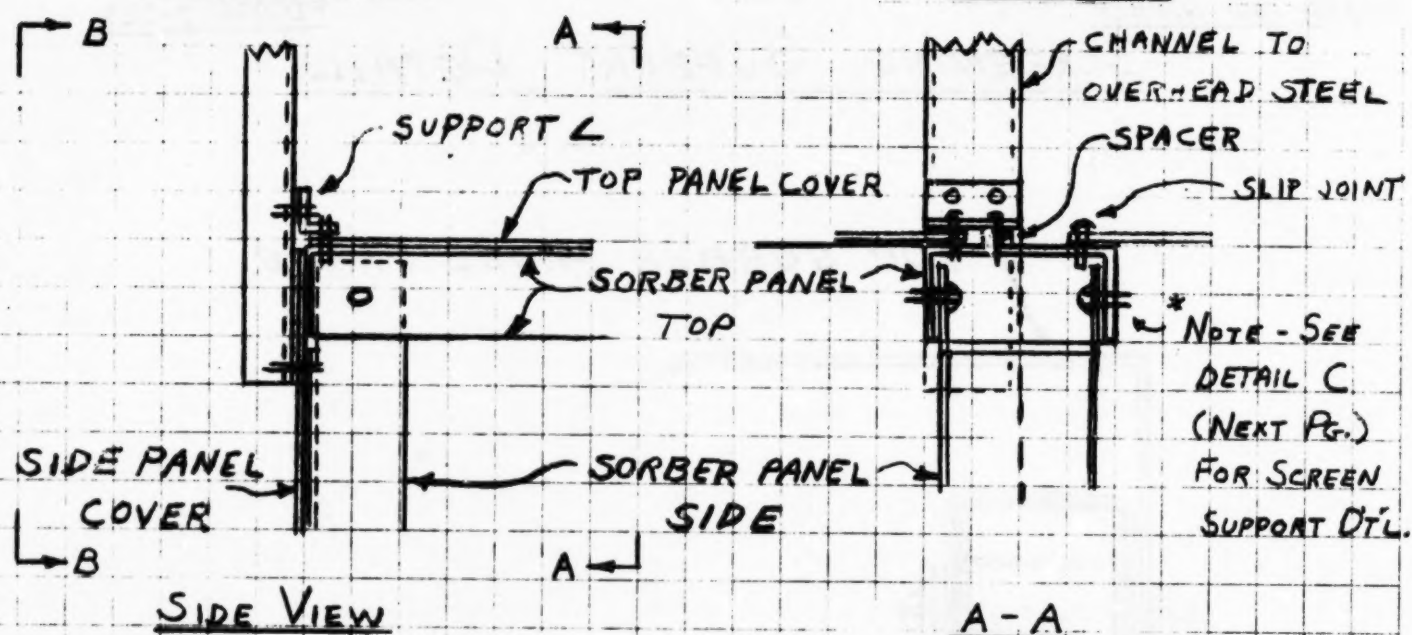
SCREENING SUPPORT DETAIL



DETAIL C

FIXED BED SORBER

FIGURE J-112



SORBER PANEL SUPPORT DETAIL

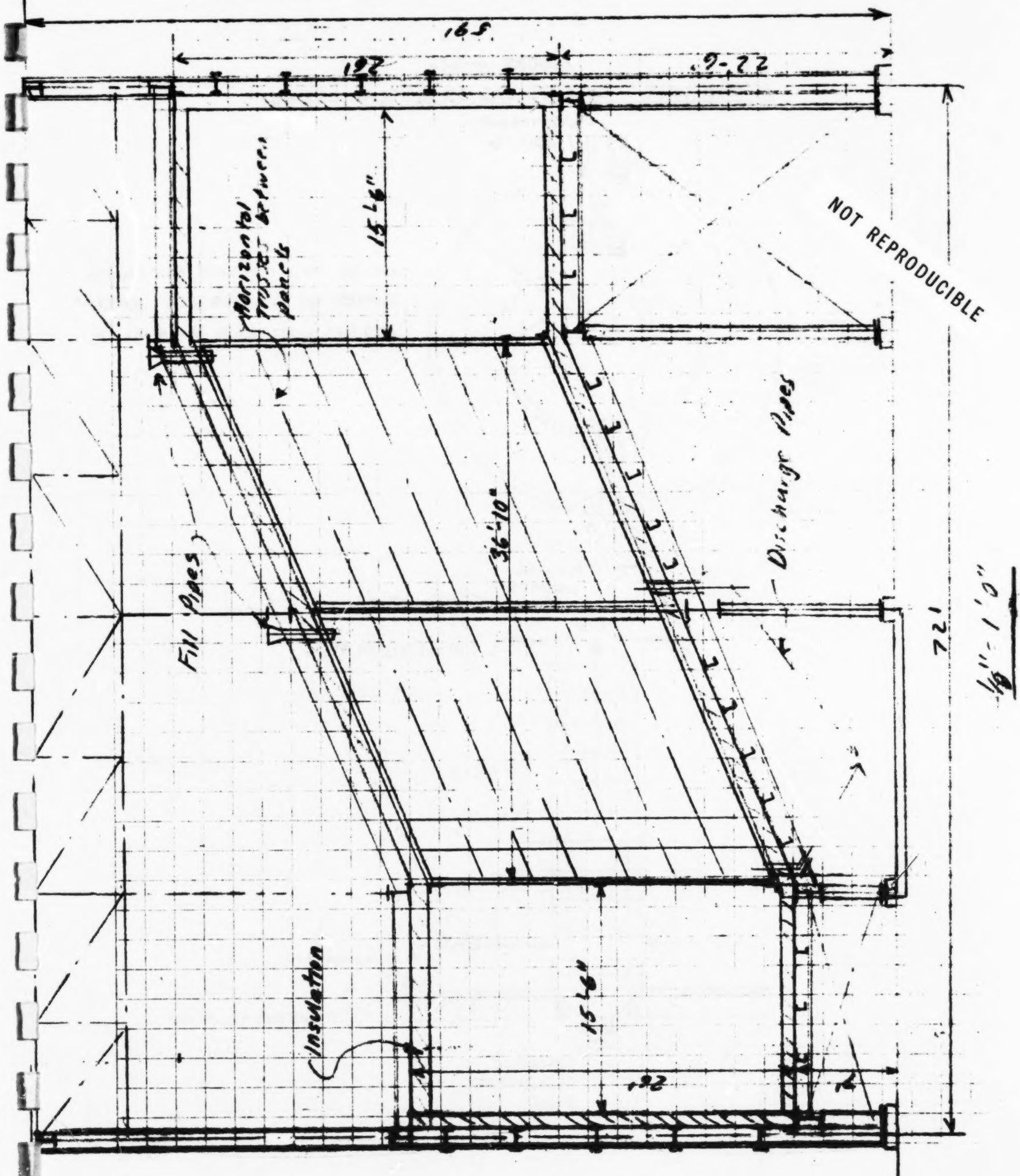
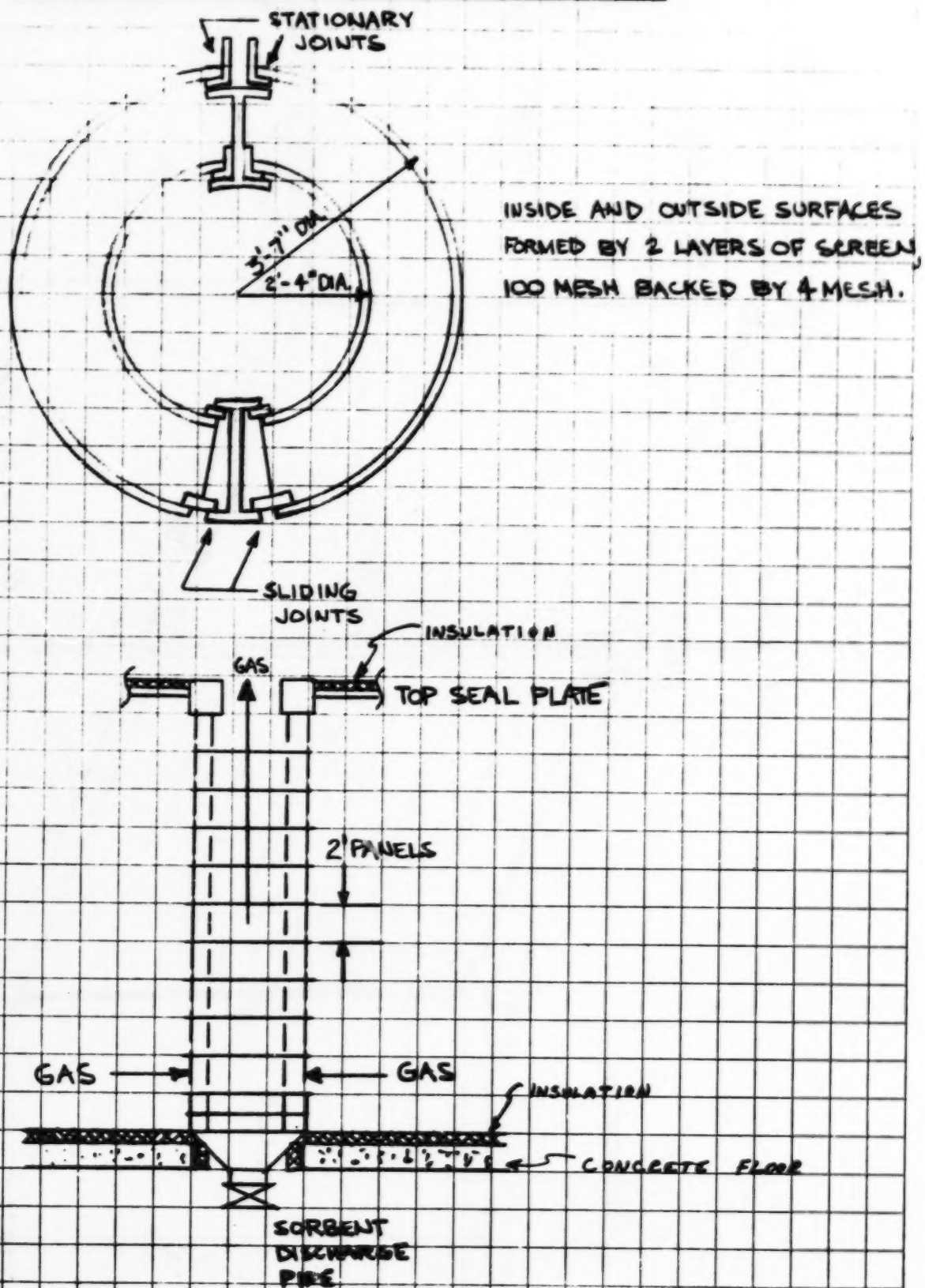
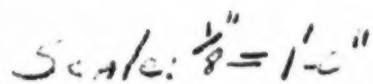


FIGURE J-115

SORBER UNIT - CYLINDRICAL OR ANNULAR DESIGN





APPENDIX K

SAMPLE CALCULATION: HEAT TRANSFER OF ALKALIZED ALUMINA IN GAS STREAM

When the solids cooler was deleted and the hot regenerated solids returned directly to the reactor, it was assumed that the sorption reaction would not take place until the solids had reached the equilibrium temperature. The time (and consequently reactor height) needed for heat transfer was calculated using several different methods and sample calculations for these methods are shown in this Appendix. For these examples the temperature of the regenerated solids entering the reactor is 1330°F, which was the preliminary design figure, instead of the final design value of 1355°F. The equilibrium temperature of 658°F is unchanged. However, since the calculated time and reactor height varies from method to method, and since the sorption reaction will likely start at some temperature above 658°F, no allowances were made for the higher solids inlet temperature.

SAMPLE CALCULATION: EQUILIBRIUM HEAT TRANSFER TIME
FOR ALKALIZED ALUMINA PARTICLES IN FLUE GAS STREAM

BASIS: Dispersed Phase Reactor, superficial gas velocity =
25 ft/sec.

TEMPERATURE: Solids : 1330 + 658°F
Flue Gas: 658 + 600°F

AVERAGE PARTICLE SIZE: 1410 microns (0.00462 ft)

PARTICLE DENSITY: 70 lbs/ft³

THEORETICAL SETTLING VELOCITY: 22 ft/sec

REF: Bird, R.B., Stewart, W.E., and Lightfoot, E.N.,
TRANSPORT PHENOMENA, Wiley & Sons, Inc.,
New York, 1960, pp. 357-360.

$$B = \frac{V_f \rho_f C_{Pf}}{V_s \rho_s C_{Ps}} = \frac{W_f C_{Pf}}{W_s C_{Ps}}$$

continued

where:

W_f = flue gas flow rate, lbs/hr

W_s = solids flow rate, lbs/hr

C_{p_f} = flue gas heat capacity, Btu/lb °F

C_{p_s} = solid heat capacity, Btu/lb °F

$$\therefore B = \frac{4,274,341 (7.69/29.62)}{330,585 (0.29)} = 11.58 \quad \text{(Data from Flow Sheet P3197-D)}$$

$$(1 + B) \left(\frac{T_f - T_o}{T_1 - T_o} \right) \quad \text{where: } T_o = \text{initial fluid temperature}$$

$$T_1 = \text{initial solids temperature}$$

$$T_f = \text{fluid temperature @ time } t$$

$$\therefore (1 + B) \left(\frac{T_f - T_o}{T_1 - T_o} \right) = 12.58 \left(\frac{658-600}{1330-600} \right) = 0.9995$$

From Figure 11.1-4 (extrapolated): $\frac{a_s t}{R^2} = 0.31$

where: $a_s = \frac{k_s}{\rho_s C_{p_s}}$

continued

$$\therefore t = \frac{0.31 R^2 (3600)}{a_s} = \frac{0.31 R^2 \rho_s C_{p_s} (3600)}{k_s}$$

where:

k_s = solid thermal conductivity, Btu/hr-ft-°F

ρ_s = solid particle density, lbs/ft³

R = particle radius, ft

t = equilibrium time, sec

$$\therefore t \text{ (sec)} = \frac{0.31 (0.00231)^2 (70) (0.29) (3600)}{k_s} = \frac{0.12}{k_s}$$

Thermal Conductivity of Al₂O₃

Reference	k_s , $\frac{\text{Btu}}{\text{hr-ft-OF}}$	$t \text{ (sec)} = 0.12/k_s$
Lange's Handbook of Chemistry	0.392	0.31
TPRC Tables	0.087	1.4

. Gurney-Lurie Chart for Spheres

REF: McAdams, W.H., HEAT TRANSMISSION, 3rd ed.,
McGraw-Hill Book Co., Inc., New York, 1954, p. 40

$$Y = \frac{t_a - t}{t_a - t_b} \quad \text{where: } t_a = \text{temperature of surroundings}$$

$$t = \text{temperature @ time } \theta$$

$$t_b = \text{original temperature of solid}$$

$$t_a = \text{flue gas average temperature} = 629^\circ\text{F}$$

continued.....

$$\therefore Y = \frac{629-658}{629-1330} = 0.041$$

$$n = \frac{r}{r_m} \quad \text{where: } r_m = \text{sphere radius}$$

r = radius from center to particular point

The entire sphere is to be cooled down to 658°F

so $r = 0$, the center point.

$$\therefore n = 0$$

$$m = \frac{k_s}{r_m h} \quad \text{where: } k_s = \text{solid thermal conductivity, Btu/hr-ft-}^{\circ}\text{F}$$

h = heat transfer coefficient between surroundings at t_a and surface (fluid to particle heat transfer coefficient), Btu/hr-ft- $^{\circ}\text{F}$

REF: Treybal, R.E., MASS TRANSFER OPERATIONS, McGraw-Hill Book Co., Inc., New York, 1955

From page 55, Curve #4 for flow of gases past single spheres:

$$\frac{hD_p}{k_f} (10^{-3}) = 0.00058 \left[Re_f (Pr_f)^{2/3} \right]^{0.52}$$

where: D_p = particle diameter, ft

k_f = flue gas thermal conductivity, Btu/hr-ft- $^{\circ}\text{F}$

continued

$$\text{and } Re_f = \frac{D_p (V_{SLIP}) \rho_f (3600)}{\mu_f}$$

where: V_{SLIP} = Slip Velocity = sorber superficial gas velocity-particle settling velocity, ft/sec

ρ_f = flue gas density, lbs/ft³

μ_f = flue gas viscosity, lbs/ft-hr

$$Re_f = \frac{0.00462 (3) (0.04) (3600)}{0.07} = 28.51$$

$$Pr_f = \frac{C_{p_f} \mu_f}{k_f} = \frac{0.26 (0.07)}{0.024} = 0.758$$

∴ Treybal Equation becomes:

$$h = \frac{0.024 (0.58)}{0.00462} \left[(28.51) (0.758)^{2/3} \right]^{0.52}$$

$$h = 15.6 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F}$$

$$\theta = \frac{x \rho_s C_{p_s} r_m^2}{k_s}$$

continued

where: θ = equilibrium time, sec

X = value from Gurney-Lurie Chart,
Figure 3-7, McAdams

$$\therefore \theta (\text{sec}) = \frac{X(70)(0.29)(0.00231)^2(3600)}{k_s} = \frac{0.39X}{k_s}$$

k_s (Btu/hr-ft-°F)	h (Btu/hr-ft ² -°F)	$m = \frac{k_s}{r_m h}$	X (Fig. 3-7, extrapolated & interpolated)	$\theta = 0.39X/k_s$ (sec)
0.392	15.6	10.9	12.1	12
0.087	15.6	2.4	2.78	12.5

. Particle Heat Balance

Solids : 1330 + 658°F

Flue Gas: 658 + 600°F

$(\Delta T)_{LM}$: 250.6°F

$$Q = mC_p \Delta T = UA(\Delta T)_{LM}$$

$$Q = \rho_p V_p C_p \Delta T = hA_p (\Delta T)_{LM}$$

where: ρ_p = particle density, lbs/ft³

V_p = volume of one particle, ft³

continued

C_p = particle heat capacity, Btu/lb-°F

ΔT = particle temperature drop, °F

$(\Delta T)_{LM}$ = log mean temperature driving force, °F

A_p = surface area of one particle, ft²

$$\rho_p V_p C_p \Delta T = 70 (V_p) (0.29) (672) = 13,641.6 V_p \text{ Btu}$$

$$h A_p (\Delta T)_{LM} = 15.6 A_p (250.6) = 3909.4 A_p \text{ Btu/hr}$$

$$V_p = (\pi/6) (0.00462)^3 \text{ ft}^3 \quad (\text{particle assumed to be spherical})$$

$$A_p = \pi (0.00462)^2 \text{ ft}^2 \quad (\text{particle assumed to be spherical})$$

$$V_p/A_p = \frac{0.00462}{6} = 0.00077 \text{ ft}$$

$$\therefore \text{Equilibrium Time} = \frac{13,641.6 (0.00077) (3600)}{3909.4} = 9.7 \text{ sec}$$